

THE CHEMISTRY AND PHYSICS OF CLAYS AND OTHER CERAMIC MATERIALS

By ALFRED B. SEARLE

CONSULTING EXPERT ON CLAYS AND CLAY PRODUCTS
LECTURER ON BRICKMAKING UNDER THE CANTOR BEQUEST

and REX W. GRIMSHAW

B.Sc. Ph.D. F.R.I.C. F.I.Ceram.

DIRECTOR OF RESEARCH AND DEVELOPMENT • LEEDS FIRECLAY CO LTD
FORMER LECTURER IN CERAMICS AND REFRACTORY MATERIALS • UNIVERSITY OF LEEDS AND
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ALFRED B. SEARLE AND REX W. GRIMSHAW

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PREFACE TO THE THIRD EDITION

IN the twenty-five years which have elapsed since the publication of the Second Edition of the *Chemistry and Physics of Clays*, all branches of science and technology have advanced to an almost unbelievable degree. The increased knowledge of ceramic materials has led to a new technical science, a fact recognised by many Universities and Colleges which now include 'ceramics' as part of their curriculum.

Although ceramics have been part of man's inheritance since prehistoric times, the last few decades have witnessed a remarkable advance in many aspects of their manufacture and application, due in the main to physico-chemical studies of the fundamental nature of the basic materials and their behaviour at high temperatures. The classical work of Bragg on the crystal structure of silicates, the applications of colloidal science and a more thorough understanding of the implication of phase equilibrium and reaction kinetics have all contributed to the increased knowledge of ceramic materials. The old rule-of-thumb methods of control are now being replaced by scientific processes, which although, unfortunately supplanting the craftsman, are undoubtedly opening the way to precision methods of manufacture. Despite the advances which have been made in the scientific approaches to ceramics, the older branches of the industry have, in the main, been the least to benefit. The next few years will be critical for the ceramic industry as a whole, especially that based on clays. The advent of competitive materials which are mass-produced and the changing standards of modern civilisation demand a new approach, both to the type of product and the methods of manufacture, which can be achieved only by a clearer and more detailed understanding of basic principles.

When I was approached by Mr. Searle to assist in the preparation of a new edition of the *Chemistry and Physics of Clays*, I was indeed honoured, and it has been a great personal pleasure to be so closely associated with one of the pioneers of ceramic science. Unfortunately a serious eye complaint has prevented Mr. Searle from making the contribution which he would have wished but, nevertheless, his encouragement and advice have been given unsparingly and to the full. Although the onus of compiling and the arrangement of the subject matter has had to be my entire responsibility, I sincerely hope that sufficient of the character and emphasis of the original editions have been retained.

To present an up-to-date picture of the physico-chemical aspects of clay and ceramic materials, of necessity, the subject matter must emphasise the importance of recent discoveries. Modern science, with the ramifications of crystal structure and mathematical theory is indeed a complicated subject, but, in keeping with the objects of previous publications by Mr. A. B. Searle, the present volume is designed to be of help to those with but a basic knowledge of science. At the same time, it has been compiled to cover the requirements of students of ceramics to full degree level in both Great Britain and the United States of America. The subject matter also is

sufficiently comprehensive to embrace the basic science curriculum of the professional degrees of the Institute of Ceramics.

I am indebted to many present and former colleagues for their help and guidance in the preparation of this volume. To Professor A. L. Roberts of the University of Leeds and to Professors F. A. Hummel and W. A. Weyl of the Pennsylvania State University, I am particularly grateful for their stimulating discussion and advice. Much of the proof-reading and the compilation of the index has been undertaken by my wife, who, at all times, has given every help and encouragement. Amongst others who deserve particular mention are Dr. C. T. Cowan for his help with diagrams and Mr. P. Kirk who assisted with the final checking and reading of the proofs.

REX W. GRIMSHAW

PREFACE TO THE SECOND EDITION

SOME years ago I endeavoured to follow Michael Faraday's method of 'selecting, co-ordinating, and publishing all the important facts that appertained to the advance of Chemistry and Physics in relation to clays and allied materials', and the first edition was one result of such effort. So rapid has been the increase in the amount of information on the Chemistry and Physics of Clays and other ceramic materials in the ten years since the first edition of this work was published that it is impossible for anyone to be engaged in active work and at the same time to read every statement on this vast subject, for the multiplicity and the kaleidoscopic diversity of chemical and physical theories constitute a phenomenon probably without parallel in recent scientific work. It has been said that the stream of serious articles and books having some bearing on the chemistry and physics of ceramic materials continues at the rate of more than five thousand a year. I need not say that I have not been able to keep abreast of this torrent; I have not even ventured to verify the estimate.

The ceramist who wishes to keep fully informed cannot simplify his task by selecting any single publication or any one theory without being liable to read too little and to miss much that would be of service. Yet, it is essential that some selection must be made in order to bring the more important facts and conclusions within the compass of a single volume. Some of the theories mentioned are of significance today, but the ceramics of the future will probably develop along lines as yet dimly foreseen. Moreover, ceramists are mainly practical men to whom theories are only of interest in so far as they are 'useful'. It seemed, therefore, both unwise and unnecessary to delay publication until there is complete agreement among leading chemists and physicists, even on such everyday subjects as the cause of plasticity, the chemical constitution of clay, and the precise nature of colouring agents in many clay products.

It is, surely, better to attempt to summarise the present state of knowledge of the subject—even if imperfectly—than to leave those in search of knowledge to flounder helplessly in an inchoate mass of articles and books, or to attempt, without any assistance, to find out laboriously for themselves what has already been found by others.

That much has been omitted is inevitable, but it is hoped that the present edition—which has been largely rewritten—will contain the greater part of the information required by those who wish to apply a knowledge of chemistry and physics to the clayworking industries, or to undertake research on these subjects. The fact that the first edition sold out rapidly encourages the author to hope that this second edition may prove to be even more useful than its predecessor.

ALFRED B. SEARLE

PREFACE TO THE FIRST EDITION

THE clay-working and allied industries are exceedingly old and have reached a remarkable state of perfection in craftsmanship, aided by only very little scientific knowledge. Within the last forty years, however, and especially during the last decade, increasingly stringent demands have been made by users of electrical and chemical pottery and refractory materials, and manufacturers of paper, textiles, and other materials in which clays are used, so that inherited and artistic skill is no longer sufficient, and Science must contribute to that knowledge of causes and effects on which future developments in these industries must depend.

Only those who have devoted special attention to the subject can be aware of the importance of the applications of both physics and chemistry to the industrial uses of clays and other ceramic materials. Such applications are so extensive, that it is remarkable that no volume has previously been published in which they are dealt with in a systematic manner, for there is scarcely a branch of physics or of inorganic chemistry which is not of value when applied to the treatment of clays, allied materials, and the products made from them, and the more intense such application, the greater is, and will continue to be, the benefit to all concerned.

It may well be asked why those engaged in such extensive and important industries as those connected with the manufacture or use of ceramic materials have paid comparatively little attention to the fundamental scientific principles involved, and why so many advanced students of Science have largely neglected the study of clays and other ceramic materials? The answer to such questions is threefold: (*a*) physicists have chiefly concerned themselves with the properties of matter in mass; (*b*) students of pure chemistry, on the other hand, have chiefly dealt with the atoms and molecules of substances of a simpler character, the reactions of which can be more easily controlled, and whose properties and relationships can be studied in a more direct manner; and (*c*) most manufacturers and users have scarcely realised, as yet, the enormous importance, to them, of chemists and physicists with a highly specialised knowledge of these materials.

The difficulties experienced in obtaining perfectly pure substances, the general insolubility and apparent inertness of most ceramic materials at temperatures below a dull-red heat, and the impossibility of obtaining many of them in some readily recognisable form—such as crystals of convenient size—have hindered research, but as these difficulties are overcome, and more and more information regarding the constitution and properties of these materials and products is obtained, great technical advances will be made.

The field of research in this subject is so vast, however, that it will be many years before it is fully occupied. At present, many important fundamental principles still need to be investigated, and far too little is known of what may appear to be such simple matters as the effect of the texture of many ceramic products,

the causes and control of their strength, the distribution of the water in partially dried articles, and the relief of the various strains which are produced during the drying and burning of many pieces of pottery, or of other ceramic articles used in the construction of furnaces, coke-ovens, sanitary appliances, etc. The causes and prevention of distortion afford another wide field of investigation which has, as yet, scarcely been entered, and the complexity of the problems of chemical equilibrium in relation to ceramics is such that only the simplest cases are, as yet, reasonably well understood. Far too little attention has been paid to the enormous influence of the size of the particles on the progress and nature of chemical reactions and of the physico-chemical changes which occur on heating clays and allied materials; and the study of such phenomena is, as yet, in its infancy. Colloidal phenomena also appear to offer almost endless opportunities for gaining further knowledge of the nature of clays and allied materials.

It will also be seen, in the following pages, that the chemical constitution of clays offers most fascinating problems, the complete solution of which has, so far, baffled the ablest chemists who have studied them, and a similar remark is equally applicable to increasing the plasticity of clays and to many of the other problems in physics and chemistry, with which those concerned with ceramic materials are in constant contact. Under these circumstances it will be obvious that the present volume is not intended to be an exhaustive treatment of the subject, but to provide, in a convenient form, such a description of the properties of various ceramic materials and articles, and of the application to them of the more important principles of chemistry and physics, as will be equally useful to students, manufacturers, and users. Several subjects of purely academic interest—such as the quantum theory and entropy—have been purposely omitted, as to have included them would have made the book unwieldy, without adding correspondingly to its usefulness.

Finally, the author wishes to acknowledge the zealous and skilled assistance of several members of his staff, without which this volume could not have been written. In this respect, he is specially grateful to Mr. W. L. Emmerson, who has taken a large share in collecting data, made many useful suggestions and read the proofs, and to Mr. F. Stones, who has assisted in other ways, including the compilation of the Index.

ALFRED B. SEARLE

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CHAPTER I

THE NATURE OF CLAYS AND OTHER CERAMIC MATERIALS

CERAMIC materials are chiefly of a mineral nature, consisting mainly of silica, alumina, lime, magnesia, iron oxide, soda, potash and compounds of these substances. For special purposes other compounds are employed, so that nowadays the scope of the subject is almost unlimited. Many oxides or other mineral forms of the rarer elements are of value as high-temperature refractories, or in other industrial applications. Various oxides are used to impart colour either to the articles or to glazes applied to them and these too are regarded as ceramic materials.¹

The word *ceramics* is derived from the Greek *keramikos*, which literally translated means *earthen*. So ceramics may be defined in a general sense as 'materials and articles made from naturally-occurring earths'. A more complete definition proposed by F. Singer states that 'ceramic is a term used to include all products made of inorganic materials which are first shaped and then permanently hardened by heat'. Ceramic articles differ from most others in that the highest temperature to which they are normally subjected is at the last stage of their production instead of at a much earlier stage. For instance, glass and most metals and alloys are first melted and are not shaped until they are at a much lower temperature and as such would not fit into the definition of ceramic materials. Glass is normally considered within the scope of the subject, however, because the glassy phase is of common occurrence in many fired bodies.

Since the earliest times, man has recognised that clay can be modelled, thrown or moulded and then transformed into a hard, dense, permanent shape by the action of heat. So 'ceramics' is largely synonymous with pottery and other articles made of burned clay. In recent years, the development of a wide range of articles from natural earths and rocks² other than clay has extended the scope of the definition; it is still true, however, that clays are, by far, the raw material most extensively used in the manufacture of ceramic articles.

Clay cannot, at present, be defined in precise terms. The word has a popular and also a series of technical and legal meanings, which are useful but not identical; so that a farmer's or agricultural chemist's concept of clay may be rejected by a potter, a brick manufacturer, a judge or a ceramist.³

In the popular sense, clay is a finely-grained rock which becomes sticky when wet. Potters and others interested in ceramics apply the term to substances which are plastic or which can be made plastic by suitable treatment and the addition of

¹ For a list of the chief raw ceramic materials and the products made from them, see p. 39.

² A *rock* is any mineral or aggregate of minerals which forms an essential part of the earth and shows a well-marked individuality (see p. 49).

³ A *ceramist* is a person engaged in the use or scientific investigation of clays and other ceramic materials.

water. Chemists and physicists define *clay* as an admixture of certain mineralogical species; such a concept is both convenient and valuable, but may be misleading in some instances.

A concise definition of clay by the American Ceramic Society is as follows: 'Clay is a fine-grained rock which, when suitably crushed and pulverised, becomes plastic when wet, leather-hard when dried and on firing is converted to a permanent rock-like mass.'

In seeking a definition of clay, it is essential to bear in mind the precise purpose for which the definition is required, the nature of the operations to be applied to the material and the use to be made of it. This may be unscientific, but any attempt at a single definition of clay which will be equally satisfactory to all who have to deal with it and other ceramic materials, may lead to confusion or to wholly erroneous conclusions.

In the present volume, the word *clay* is chiefly used as meaning the natural material either as found, or after such processes of cleaning, purification or preparation as it may have undergone. When a highly-purified clay is being considered, its essential constituent is termed *clay substance* or *true clay* (or in some instances *clay mineral*) according to which best suits the context.

THE HISTORICAL DEVELOPMENT OF CERAMICS

SOME idea of the relative importance of the different types of ceramic materials may be gained from a study of their historical development.

The discovery of ceramics ranks as one of man's earliest scientific achievements.

Some enthusiastic ceramists claim that theirs was the first Science, for in Genesis there is the statement that 'God made man from clay'. Perhaps if this is not sufficient to prove that ceramics is the earliest science, it does suggest that at least it was the earliest technology.

The early history of man is traced mainly through his ceramics. All ancient settlements left traces of their existence only through indestructible material. Wood and cloth have vanished; only pottery, flint, bricks, stone products and some metal articles (chiefly gold, copper and bronze) have survived the rigours of thousands of years. From a study of these we can often visualise the modes of life of our early forbears.

The earliest traces of primeval man are to be found in the clay on which he walked. Footprints, baked hard by the sun, have remained as such up to the present day. Clay will stick to most things with which it comes into contact. An early development seems to have been the cementing of a wood and grass framework by clay, and this probably led to the manufacture of rough sun-dried bricks. These were serviceable in dry weather and could resist showers, but not prolonged heavy rain.

Then one day came the *fire*, and the clay body was converted into a hard mass, indestructible by water. Later, deliberate burning would follow and then the making of special fired-clay shapes for drinking vessels and other utensils. Ceramics had been born.

The exact date can never be known with certainty, but it is possible that simultaneous discoveries of fired clay-ware were made in several parts of the world. Crude vessels of burned clay have been unearthed in England, Belgium, Germany, North and South America, Egypt, Mesopotamia and elsewhere, dating back to about 5000 B.C.

The development from these first crude shapes to the beautiful, glazed articles of the later civilisations was slow and can be traced only with difficulty.

Egypt has produced pottery discovered on the sites of old tombs, dwellings and temples, which has proved very illuminating. Terra-cotta vases, probably used to contain provisions for the dead, can be ascribed to the Memphite period (5000–3000 B.C.). Although these are of crude clay they are of exquisite shape, and so highly polished that they appear glazed. Undoubtedly the Egyptians had learned the art of glazing by 3500 B.C., for decorative tiles have been found with a blue copper glaze covering a body of sandy clay. Some insight into the methods of these early potters has been given by the tableaux on the walls of the tombs depicting scenes from everyday life in the Theban period (3000–1700 B.C.). Later, the Egyptians also knew how to make glazed earthenware, for many beautiful decorative pieces have been found in the pyramids and temples.

In **Babylonia and Assyria** among the ruins of the cities of the ancient civilisation of Mesopotamia are to be seen many examples of the art of pottery-making, using crude clays as raw material. A feature of this period is the large single-piece ware, made with high precision. The British Museum possesses coffins made of clay which have been enamelled with different colours.

Persian pottery was a natural successor to the Assyrian. Coloured glazes were developed by adding metal oxides to an alkaline base. There are undoubted examples of ware made on an early type of potter's wheel. The early Indian races almost certainly copied Persian methods, for much of their produce is of similar type.

Early Grecian civilisation is remarkable for the contribution it has made to the Arts and Sciences; in the field of Ceramics, the Greeks departed from the conventional methods of earlier workers and specialised more on delicacy of shape than on heavy glazed ware.

They covered their ornate pieces with a thin transparent gloss, which was acidic in character. To achieve exquisite shape they must have purified the clay by washing and sieving, thus producing a fine-textured material from which the larger particles had been removed.

The **Ancient Romans** were great empire-builders and architects, and although they did produce some pottery with rich ornamentation in Grecian style, their real contribution to Ceramics is in large-scale work. They specialised in bricks and tiles, and many of their buildings (largely of brick) are preserved to this day. They made baths, aqueducts, drain-pipes and even vitrified stoneware pipes which were shaped at the ends so that they could be fitted together and then cemented into place. Wherever the Romans travelled, they took their ceramic art, and there is one remarkable fact—the ware is always similar and independent of the locality in which it is found; its colour, texture and density vary but little. Roman pottery is characterised by two different types:

- (a) *Samian ware*, which is red;
- (b) *Etruscan ware*, which is black and not so abundant.

On the decline of the Roman Empire, Ceramic Art in Europe also fell into a state of decay, and so remained for many centuries.

Far Eastern Ceramic Ware. The first records of bricks and tiles being made in China relate to the period of the Emperor Wu (140–88 B.C.), though legends infer a much earlier date. Historians¹ have stated that the first pottery articles produced in China were made about 2500 B.C.; these were crude, and fine Chinese pottery does not date back further than 200 B.C. Ceramic ware has been associated with the various Dynasties of Emperors:

(a) The *Han Dynasty* (206 B.C.–A.D. 220) is noted for its stoneware type with a brown or bluish-green glaze and for the invention of the potter's wheel in China. Attempts to make porcelain by applying imported ground glass yielded a poor product and the firing temperature was much too low.

(b) The *Sui Dynasty* (A.D. 581–617) witnessed the appearance of the first translucent porcelains and other ceramic wares. Opaque, glossy chinaware was made from kaolin. The early part of this Dynasty is regarded as the Great Period of production of Celadon (green) ware.

(c) The *Tang Dynasty* (A.D. 618–906) saw great advances in porcelain and stoneware sculptures. A much higher firing temperature was used and the quality of the porcelains produced was thereby greatly improved. About this time, pottery manufacture had a great fillip in China with the advent of ceremonial tea-drinking and the consequent necessity for many cups.

(d) The *Sung Dynasty* (A.D. 960–1280) produced finer bodies and a greater variety of glazes and colourings. During this Dynasty, porcelains of delicate appearance and good quality were produced and new designs in shape, colour and decoration were employed. For these reasons, this period is regarded as a golden one in the history of pottery and porcelain in China. The export of ware to Europe began and was known (from its place of origin) as *chinaware*.

(e) The *Ming Dynasty* (A.D. 1368–1643) represents a period in which ceramic wares attained a high degree of delicacy of product and decoration and technical perfection. Beautiful examples of overglazed porcelains made in this period are much sought after to this day.

(f) The *Manchu Dynasty* (A.D. 1643–1912) appears to have included two or more minor dynasties:

(1) The *K'ang-Hsi Dynasty* (A.D. 1662–1722) saw an increase in the standard; in it were developed coloured glazes of a quality which surpasses our present-day endeavours.

(2) The *Yung Cheng* and *Ch'ien Lung Dynasties* (A.D. 1723–95) are remarkable for the close similarity of manufacturing methods to those of the present day. Wood-fired kilns were used, which may account for the perfection achieved in glaze colouring.

¹ Li Ch'iao-p'ing, 'The Chemical Arts of Old China', *Journal of Chemical Education* (Easton, Pa., U.S.A., 1948).

Although the latter part of the Manchu Dynasty saw a period of marked decline, the porcelains retained their great reputation and the industry flourished into the early years of the twentieth century.

Japanese pottery was a natural development from Chinese ware. The Japanese extended the scope of 'ceramics' and became famous for 'egg-shell' and thin-sectioned translucent chinaware. They were probably the first to use lead-borax glazes.

European pottery (apart from the crudest earthenware) almost ceased to be made after the withdrawal of the Roman legions and so continued until the Arabs and Saracens brought the art to Spain. They introduced ware with a porous body of clay covered with a white, opaque glaze of high lustre. *Majolica ware* was made originally on the Isle of Majorca, but its manufacture spread throughout Europe, especially to Italy. Many Italian artists devoted themselves to Ceramics in the fifteenth century and a characteristic style emerged, known as *faience*, after the town of Faenza where the industry was centred. The French exploited this kind of ware to the full in the seventeenth and eighteenth centuries. Excellent clays for the production of porous pottery were common in many parts of France and ware with a matt glaze, containing tin, became very popular.

The development of *porcelain* in Europe about the end of the eighteenth century brought about a decline in the popularity of *faience*. The Dutch also mastered the art of manufacturing *faience*, but they, too, suffered from the competition of foreign porcelains. True porcelain was first produced in Europe by the Germans, who, after the discovery of local white kaolin, closely followed Chinese methods and established the porcelain industry at Dresden and elsewhere.

British pottery was relatively slow to develop. The 'Cistercian ware', thought to have been made by monks of the sixteenth century, has a coarsely-grained body with a heavy glaze. *Slip-ware* was manufactured in Staffordshire in the seventeenth century by the famous brothers Toft and others; although rather crude in design, this ware represents a great step forward in ceramic technique and is therefore prized by collectors. Following the introduction of the *Majolica* industry at Lambeth by the Dutch, Dwight produced a type of salt-glazed porcelain, which proved superior to the German counterpart. A few years later, around 1690, the Elers brothers used washed Staffordshire clays for making dense ware, but it was not until well into the eighteenth century that china clay was used to give whiter earthenware bodies. Once this step had been taken, English chinaware progressed at an amazing rate, so that at the beginning of the nineteenth century, with the introduction of bone china, it became world-renowned. In recent years, the trend has been towards more mechanisation and precision of ware than to new materials or bodies.

American pottery has developed on distinctive lines. The primitive pottery of South America does not differ materially from other primitive wares although it has distinctive styles of decoration not found elsewhere. The same may also be said of the 'Indian' earthenware, which is typified by a heavy, brightly-coloured glazing. The modern pottery industry of the United States was brought in by European emigrants, but an individual style emerged which was dictated largely by the types of clay and the needs of a rapidly-expanding populace. Ceramic ware developed along rather different lines from those in Great Britain and resembled more closely

that of Central and Western Europe. In recent years, intensive research has led to a great improvement in body and glaze compositions, so that, despite the lack of suitable, easily-accessible china clay, modern American pottery is of excellent quality.

There is a very large and intensive literature on Ancient and Historical Ceramic Wares and any reader interested in this aspect of the subject should refer to it; the present volume is mainly concerned with the chemistry and physics of ceramic materials and articles. Clay, however, as a survey of the modern pottery industry shows, is still the all-important raw material.

IMPORTANT CERAMIC ARTICLES AND MATERIALS

TABLE I.I shows the chief ceramic products and the materials from which they are made. Minerals and other substances shown in brackets are sometimes used to impart special properties or to modify undesirable ones, such as excessive shrinkage during drying or firing, low resistance to high temperatures or to thermal shock.

Structural Clay Products. Articles made chiefly of clay and used in the Building Trades and in Civil Engineering are commonly known as 'Structural Products'; they include what is generally known as The Heavy Clay Industries.

In addition to the articles mentioned in Table I.I this group includes acid-resisting bricks, tiles, tanks and pipes used in the chemical industries and to some extent in others, such as leather manufacture and in a variety of articles used in the transmission of electricity such as cable conduits and insulators.

Clay products for the retaining or exclusion of heat at low or moderate temperatures are also included, but those used at higher temperatures are included in 'Refractories'.

Refractory Materials. Firebricks and other materials, which are chiefly used because of their great durability at high temperatures, have been in use since about 2000 B.C., but those which are now known specifically as *refractory materials* (colloquially *refractories*) have only been recognised, as such, for about 300 years and some of them for less than a few decades. This is because the need for materials to resist very high temperatures arose only with the development of the metal-smelting and the glass-melting industries.

At first, stones of moderate heat resistance were utilised, then the superior quality of bricks made of certain *fireclays* was realised. About 200 years ago, *silica bricks* made of *ganister* and other silica rocks were found to be particularly suitable for furnaces used in steel-making, and still more recently basic materials, such as *magnesite*, *dolomite* and *chromite*, were introduced. With the coming of the Jet-engine and Atomic Ages, even more problems have had to be solved and the new developments include the manufacture of articles made from sintered oxides, other highly-refractory bodies and combinations of metals and ceramic materials known as *cermets*.

The introduction of these new products has, however, been on highly specialised lines, for the main bulk of ceramic products still contain clays, sand, flint, felspar and the like as their principal raw materials.

TABLE I—I. RAW MATERIALS USED IN THE PRINCIPAL
CERAMIC INDUSTRIES

<i>Industry</i>	<i>Type of Product</i>	<i>Raw Materials Used</i>
Structural Clay	Building bricks of all types	Clay (sand, chalk)
	Hollow blocks; Terra-cotta	
	Roofing tiles and floor tiles	Clay
	Flower pots. Chimney pots and flues	
Refractories	Unglazed (land) drain-pipes	Clay and glaze (often salt)
	Glazed pipes and accessories	
	Fireclay bricks and raw fireclay	Fireclay (grog or pre-calcined clay)
	Silica- and siliceous-bricks and raw stone	Quartzite rocks, ganisters, etc.
	Magnesite bricks	Magnesium-containing ores, principally carbonates, hydroxides or from sea-water
	Chrome bricks	Chrome ores
	Chrome-magnesites	Chrome- and magnesium-ores
	Dolomite bricks	Dolomite (serpentine, talc)
	Carbon bricks	Graphite (clay)
	Silicon carbide bricks and shapes	Coke, sand (salt, sawdust)
	Insulating refractories	Clay or other refractory and combustible, e.g. sawdust
		Diatomaceous earth, vermiculite
	Sillimanite bricks	Sillimanite. Kyanite or Andalusite
	High (over 50 per cent) alumina bricks	Fireclay and Bauxite
	Retorts, Crucibles, Ladles, etc., for metallurgical, gas-plant, scientific and other applications	Bauxitic clays
Pottery	Glazed wall and earth tiles	Clays and Glaze, Pyrophyllite, Talc
	Domestic and Sanitary Earthenware	Clays, Felspar, Flint, Glaze, Cornish stone
	Bone china (chinaware)	Clays, Bone ash, Cornish stone
	Porcelain (domestic, laboratory, industrial)	Felspar
	Stoneware	Clays, Felspar, Flint
	Glazes and Engobes	Clay (fluxing agents)
Miscellaneous Ceramic Materials		Clays, Flint, Felspar, Other fluxing agents (colouring compounds)
	Fused silica	High-purity quartz crystal or sand
	Special Refractories	Pure oxides, e.g. BeO , Al_2O_3 , MgO , ZrO_2 , ThO_2 , zircon, spinels, etc.
	Electrical ware	Clays, Flint, Felspar
		Rutile (TiO_2)
		Steatite, Talc
		Magnesium and Barium Titanates
		Zircon
		Ferrites
	Cermets	Metals and Ceramic Oxides
	Glasses	Sand, Soda Ash, Limestone (felspar, sodium sulphate and nitrate, borax and boric acid, lead oxide, potassium compounds, miscellaneous colouring and opacifying agents)
	Glazes	
	Enamels	

Pottery.¹ The term *pottery* includes many varieties of ware from the crudest vessels of prehistoric times to the most beautifully decorated porcelains, stoneware and earthenware; it also includes many articles such as large grain-jars used in ancient times for storing corn and other dry materials, wine-jars and modern sanitary ware and the large tanks for containing corrosive acids. Many kinds of earthenware, stoneware and porcelains are used for scientific and experimental purposes as well as for electrical apparatus (insulators, switch-bases, sparking plugs and as bases or frames for electrical heating appliances).

As clays are the chief constituent of all kinds of pottery, they and their products are of very great importance to many industries.

Glass. Glass is not a ceramic material in the sense that articles made of it are not produced in the same way as ceramic ones, i.e. glass articles are made from molten or semi-molten glass by moulding or blowing, and (unlike pottery and other fired ceramic bodies) heating is not the last part of the manufacturing process. Various kinds of glasses are formed in the burning of many ceramic bodies (especially in porcelain, stoneware, refractory and other clay materials, and in glazes applied to certain types of pottery, bricks, tiles, sanitary ware, etc.). Any study or treatise on ceramic materials would therefore be incomplete without due consideration being given to glass.

Glass must have had its origin shortly after the first fired ceramics were produced. The fusion of sand in the ashes of a wood fire appears to have been an early observation, but difficulties arose in the shaping of the molten mass and little is known of ancient glass. Assyria and Egypt provide some of the earliest examples, but few articles can be dated back with certainty to pre-2000 B.C. Beads made from a pottery glaze about 1600 B.C. have been found, but it was not until a much later date that the art of blowing glass was discovered.

The Romans had drinking glasses in the time of Nero (A.D. 54) and by A.D. 220 this was a flourishing industry. Window glass was in use by A.D. 422.

Venice was famed in the thirteenth century for mirrors and drinking glasses of beautiful colour with unrivalled gilding and filigree work.

The first record of glass being used in England was at Monkwearmouth, where windows were installed in the Abbey in A.D. 674. The industry really started in A.D. 1557, when the first lead-flint glass was made. By 1700, the manufacture of drinking glasses superseded in quality those of Venetian origin, which were mainly of lime glass. In 1773, a factory was established at Prescott in Lancashire and thus began what is now a great industry using local sand.

The principal raw materials used in the manufacture of glass are shown in Table I.I and are discussed in more detail in Chapter VI.

Glazes. The glazes which produce a glossy surface on pottery, stoneware and other clayware are *glazes* though they differ in composition from most commercial glasses and are used for a different purpose. (See Chapter VI.)

¹ It has been customary for many years to regard *porcelain* as distinct from *pottery* largely because of its greater beauty and the mystery which was, for a long time, associated with its production. Strictly, the term *pottery* includes a series of a great variety of ware with the crudest earthenware at one end, fine earthenwares and stonewares as intermediate and porcelain at the other end of the series.

Enamels may be regarded as a variety of glazes which are suitable for use on metals. The term is also applied to some opaque glazes used on pottery and porcelain for decorative purposes.

THE GEOLOGY OF CLAYS AND OTHER CERAMIC MATERIALS

GEOLOGICALLY clays are composed of various minerals of primary and secondary origin, all of which are of a comparatively 'fine' or small grain size. Some minerals are often present in grains which are larger than those of the other minerals, but, because of the nature of their formation, true clays only infrequently contain fragments visible to the unaided eye. Clays in their natural form may consist of many different minerals, not one of which predominates. It is meaningless therefore to refer to *pure clays*. There are, however, certain minerals or classes of minerals which occur in all clays and have been termed *clay minerals*. These can be separated, by virtue of their small particle size, from the coarser-grained components in a clay and in some instances can be isolated in a fairly pure state.

Clays may be found in a variety of forms. They may occur as a soft paste (mud) or as a soft solid (mudstones) or as a laminated rock (shales). Some clays are at a great depth below the surface and may be in thick beds (some Lias clay beds are more than 600 feet thick) or as narrow seams (e.g. the *fireclays* which occur below coal seams). The china-clay deposits of Cornwall are so thick that the bottom has not been reached in some places and field tests suggest that they may be over a mile in depth. Other clays lie quite close to the surface and are, in general, termed *alluvial clays*.

Deposits of clays of all kinds are described as *argillaceous* (French *argile* = clay) to distinguish them from sandy (*arenaceous*) formations; they are also classified as *clastic* to differentiate them from the igneous rocks.

The earliest rocks to be formed were similar to the granites, diorites, and other igneous formations which have crystallised from volcanic masses. These rocks, which are termed *primary*, are rich in feldspathic, micaceous and quartzitic components and, in addition, numerous other minerals may be present. In the course of geological time, such agglomerations have been and still are being subjected to the action of air, water and other external agencies, which alter the character of the parent rock and the nature of the primary minerals. The hard, crystalline formation is broken down to a finely-grained mass of *secondary* and some unchanged primary minerals. Two main types of physico-chemical reactions have been recognised.

(i) **Hypogenic changes** are those occurring *under* the surface of the earth, usually through the agency of heat and/or chemical substances. The well-known 'kaolinisation' of granite in Cornwall is a typical example. Ascending superheated solutions, heavily charged with chemicals, probably of an acidic character (CO_2 and SO_2), were forced upwards through the granite mass. Under these conditions of high temperature and pressure, the feldspar component was largely altered to the clay mineral, *kaolinite*. The hydrolysis reaction may be expressed simply in the following chemical terms:

TABLE I—II. GENERAL TABLE OF THE EARTH'S STRATA AND GEOLOGICAL TIME-SCALE
(After Arthur Dendy, F.R.S., Arthur Holmes, D.Sc., F.G.S. and British Museum Guide to Department of Geology and Palaeontology)

<i>Era</i>	<i>Epoch</i>	<i>Depth in thousands of feet for each epoch surface</i>	<i>Age in millions of years for each epoch surface</i>	<i>Beds, Deposits, etc.</i>	<i>Important Ceramic Deposits</i>
Anthropozoic	Holocene	0-25 0-25	0-02 0-02	Present Historic Neolithic	Now being formed: silt, fluviatile, alluvial clay, sand
	Pleistocene	3-75 4	0-98 1	Palaeolithic Glacial	Boulder clay
Tertiary	Pliocene	13 17	7 8	Norfolk, Norwich and Lenham beds	Brick earths, sand, pottery, and ball-clays
	Miocene	14 31	12 20	Tortonian and Helvetian Limestones	
	Oligocene	12 43	15 35	Hemstead Bembridge Osborne	
	Eocene	20 63	25 60	Bagshot London clay Lower London Tertiaries	
Mesozoic or Secondary	Cretaceous	44 107	50 110	Chalk Greensands Wealden Purbeck	Brick-clays, sand
	Jurassic	8 115	30 140	Portland clays Oolites Cheltenham Lias	Cement-clays Oxford clays

TABLE I—II. GENERAL TABLE OF THE EARTH'S STRATA AND GEOLOGICAL TIME-SCALE
(After Arthur Dendy, F.R.S., Arthur Holmes, D.Sc., F.G.S. and *British Museum Guide to Department of Geology and Palaeontology*)

	Triassic	17	132	40	180	Lias, Marls Sandstones	Brick-clays, marl-clays, sand shales
	Permian	12	144	25	205	Limestones Red sandstone	Magnesian limestone, brick-clays
	Carboniferous	29	173	80	285	Coal, Millstone Grit Limestone	Brick-clays, fireclays ganister
	Devonian	22	195	45	330	Red sandstone	Brick-clays and shales
	Silurian	15	210	40	370	Ludlow Wenlock Llandovery Taranon	Slates, grit-stones
	Ordovician	17	227	78	448	Caradocian Llandeilan Arenigian	Sands and slates
	Cambrian	26	253	77	525	Olenidian Paradoxian Olenellian	Slates
Proterozoic	Upper Pre-Cambrian	90	343	325	850	Sudburian, etc.	Serpentines, Quartzites, Clay-slates
Archæozoic	Lower Pre-Cambrian	90	433	400	1250	Laurentian Grenville	
	Metamorphic	?	?	?	?		Mica-schist and quartzites
Azoic				1250	2500	Igneous Molten Gaseous	

permanent suspension and produce a viscous *slurry* or *slip*. Most clays possess some *colloidal properties* or can be partially converted into the colloidal state.

In the solid state, materials may be either amorphous or crystalline or mixtures of the two.

(1) **Amorphous.** An amorphous solid has no definite shape or geometrical internal structure. Many ceramic materials (especially plastic clays) appear to be amorphous even under a microscope, but the use of X-rays and an electron microscope shows that they are essentially crystalline. This may easily lead to confusion of thought as they behave in many ways as amorphous substances and in others as crystalline ones.

Formerly, the distinction between amorphous and crystalline was much more important than it is now, though it still has some valuable uses, chiefly in connection with glazes, glasses and fused materials which have cooled without crystallising (these are termed vitreous substances).

(2) **Crystalline.** A mass may consist wholly of crystals more or less perfectly developed and interlocking with each other to form a compact, impermeable material or a porous one; the difference lies in the shape and compactness of the crystals. Such structures are usually (a) the result of slowly cooling a molten material, (b) metamorphism, or (c) crystallisation from a solution; typical examples of value to ceramists are rock- and vein-quartz, quartzites, crystalline limestones, dolomite, sillimanite, chromite and sometimes magnesites. Many artificially prepared ceramic materials, such as carbides and sintered alumina, are also wholly or partially crystalline.

For a substance to be crystalline it must have a characteristic form or shape. X-rays have shown that the atoms (Chapter II) of which the mineral is composed must be arranged in a symmetrical manner throughout the mass. Crystals range in size from a few Ångstrom units¹ to several inches in size, depending on the type, composition and mode of formation.

The properties of a crystalline mass are in some ways advantageous and in others detrimental; thus, when a material occurs in this form it is often fairly pure, although there is always the possibility of isomorphous substitution. Some materials have, however, the disadvantage of undergoing changes when heated, and this may cause difficulties when they are used. A typical example of this is quartz or quartzite, which is used in the manufacture of silica bricks. When these bricks are burned, the silica is changed from the form in which it normally occurs in nature to allotropic varieties of lower specific gravity, with a consequent volume expansion. This change takes place very slowly in the case of crystalline quartz, but much more rapidly when amorphous silica is heated. Thus, the cost of heat treatment is much greater for crystalline than for amorphous silica, and the conversion is not usually so complete. For this reason, an entirely crystalline structure is not so desirable in the case of raw siliceous materials, but as this is the purest and most abundant form, it is the one chiefly used.

Where the crystalline form is stable at high temperatures, it has the advantage that it is less easily attacked than amorphous material, and therefore, bricks or other refractory articles with such a structure (e.g. sillimanite, mullite, tridymite, silicon

¹ An Ångstrom unit (1 Å) = 1×10^{-8} cm.

carbide, corundum, periclase and spinels) are more resistant than those composed of amorphous material. When the material has an appreciable coefficient of expansion, crystals are more liable to crack and cause the disintegration of the ware than are amorphous grains. From the point of view of users of refractory materials, satisfactory structures must have low thermal coefficients of expansion.

Wholly crystalline structures are fairly common amongst some raw refractory materials, but are less frequent in the finished products.¹ In the latter, there is usually some other material between the crystals; it is generally of a glassy nature. The size of the grain enables classification into (a) coarse crystalline, in which the grains are readily visible to the unaided eye, and (b) fine crystalline, micro-crystalline or crypto-crystalline, in which the particles are much finer, the last two being so fine as to require a microscope to enable the structure to be identified. A fine crystalline texture is generally preferred both in raw and refractory fired products, as it has some of the advantages of amorphous structures, without possessing in such marked degree the disadvantages of a coarse crystalline structure already enumerated. A moderately coarse structure is, however, desirable in the case of magnesite, as on calcination the carbon dioxide escapes more conveniently than from a fine-grained or crypto-crystalline magnesite. Quartzites in which the quartz grains show clear cracks are not suitable for the manufacture of refractory bricks, as they tend to be weak along these lines. This is also true of chromites, where the texture of the spinel grains is all-important.

A single amorphous or crystalline substance is termed a *mineral*,² and within wide limits, minerals have a definite chemical composition and a characteristic structure. It is uncommon in nature for minerals to occur independently; they are more frequently found in association with others. Such mixtures are known as *rocks*, which may be defined as any portion of the earth which has individuality. Although a rock is often thought of as a hard, compact material this is not correct because some soft-textured materials are termed 'rocks'.

In addition to the two states (amorphous and crystalline) which relate to the fundamental nature of individual particles in a mass, many ceramic materials exist in various types of aggregation, where grains of perhaps many sizes and mineral forms are bonded together. The chief of these are:

Agglomerates in which the particles are united to form a mass with a granular structure. These are predominantly of either crystalline or amorphous matter, held together by previously applied (natural) pressure, or they are cemented together by some form of bond which may be glassy, amorphous or colloidal. In the raw materials, the principal cementing materials are clay, quartz, opal, chalcedony, iron oxides (haematite, limonite and magnetite), carbonates of calcium, barium, magnesium and iron (calcite, witherite, dolomite, chalybite and ankerite), sulphides of iron (chiefly pyrites), hydrated silicates (zeolites, chlorites, epidote, serpentine, talc,

¹ The present trend is to increase the proportion of crystalline matter in the more important ceramic products, especially industrial porcelains, stonewares and refractory materials.

² The legal interpretation of the term 'mineral' is based on the supposed origin of the word as 'something mined or only obtainable by mining'. Hence a surface clay is not legally a mineral, though if it forms part of a mass of the same material, most of which can be obtained only by mining, it is (at any rate as regards the bulk) deemed to be a mineral. The various important legal decisions on the subject have not made the matter wholly clear.

mica), anhydrous silicates (felspar, hornblende), sulphates of calcium and barium (gypsum, barytes), and various phosphates. Of these, the commonest cement is clay or silica, but carbonates, sulphates, silicates and iron oxides are also important.

Colloidal silica cement is usually produced by the weathering of silicate rocks; the percolating waters containing the silica in solution descend until they reach a porous rock, in which the silica, being unstable, tends to separate from the solution and is deposited as a cement between the grains of the rock through which it percolates. A siliceous cement may also be formed as a result of the silica being precipitated owing to a decrease in the temperature of the solution. Many rocks are united by a calcareous cement derived from water containing carbon dioxide which has previously percolated through limestone or chalk and has dissolved some calcium carbonate. The solution is carried through the fissures and pores of other rocks until the carbonate is deposited and forms a calcareous cement.

Ferruginous cements are common in sandstones and other rocks; they appear to have been formed by the percolation of water containing ferrous carbonate or hydroxide in solution.

Gypsum acts as cement in some shales and sands. Thus, Fontainebleau sand contains sand-calcites which consist of isolated masses composed of gypsum and sand. Some of the Northumbrian fireclays are thought to be cemented by barytes.

The precipitation of cements in rocks is usually a result of one of the following actions: (a) the mingling of solutions from different sources and their mutual precipitation; (b) the chemical action between solutions and the rocks they traverse; (c) a decrease in temperature causing supersaturation; and (d) a decrease in pressure.

A ceramic material for modern high-temperature uses in which the natural cement occurs in large proportions is generally undesirable unless it is very highly siliceous or argillaceous and is itself refractory.

In the finished goods, the cement or bond produced by the burning process is usually of a very complex nature and is generally in the form of a glass composed of various silicates, alumino-silicates, etc.; in stoneware and porcelain such a bond is essential.

The larger particles or granules in a material of granular structure may vary greatly in size from that of pebbles (as in quartzitic conglomerates which are sometimes employed for the manufacture of silica bricks) to the fine, amorphous grains which comprise the bulk of most clays, these latter being so minute as to render identification impossible, even when they are examined under a microscope. The granules may be either amorphous or crystalline or an indefinite mixture of materials in both these forms.

The principal types of granular structure are as follows:

(a) *Granular Fragments in a Glassy Matrix.* These are not very common in raw ceramic materials, though they occur frequently in igneous rocks. This structure is found in porcelain, stoneware, fired silica and in some clay bricks; these consist of crystal of mullite, quartz and other forms of silica, cemented together by a glassy mass composed of various complex silicates and alumino-silicates which sometimes include minerals such as wollastonite and anorthite. The whole mass is usually

coloured by the iron compounds present. The granular matter may be either crystalline or amorphous and either coarse or fine.

(b) *Amorphous or Crystalline Fragments in a Non-glassy Matrix.* This structure is more frequent in the raw materials than in the finished products as, in the latter, the strength of the articles depends more often on the presence of some fused material to act as a bond. Many raw materials, however, consist of fragments which are cemented together by amorphous matter, which has been precipitated or otherwise deposited from solutions percolating through them.

The ideal structure of a quartzite for the manufacture of silica bricks is one in which the grains of quartz are very minute and are bound together with an amorphous cement. This is very important, as when a quartzite of this kind is heated, the elastic nature of the cement reduces the expansion of the silica to a minimum, whereas a quartzite which does not contain any cement has a very marked expansion and frequently cracks on account of the strains set up in the material. One of the most suitable quartzites used for making silica bricks is the amorphous or cryptocrystalline form found in flints and chalcedony. *Findlings-quartzit* consists of erratic boulders of minute grains of quartz surrounded by chalcedonic cement. Of similar composition is *silcrete*, a quartzite from South Africa, now used for the manufacture of high-grade silica bricks. In some cases, silica has been precipitated round irregular quartz grains and has apparently taken on the crystalline form of quartz. The Stiperstones quartzites occurring near Shrewsbury are a good example of silicification, the sand grains having been enlarged by secondary growth, though crystal faces have not developed. The Lickey, Bwlchgwyn and other Welsh quartzites are due to similar silicification, and will be discussed in detail in a later chapter. Many shales and slates are often silicified by the deposition of secondary silica in their fissures, and some limestones are probably cemented with a similar material.

Ganister is a fine-grained silica rock which may be sericitic in character. The term was originally applied to a portion of the Lower Coal Measure Series near Sheffield but it has been largely applied to other silica rocks, found elsewhere, which are not so fine-grained nor so angular, but can be used for some of the same purposes as 'true ganister' (the name applied solely to the South Yorkshire and Derbyshire material. 'The other so-called ganisters have been described by the Geological Survey as 'ganister-like sandstones' and are of a different origin.).¹

Laterites appear to be amorphous mixtures of hydroxides, of iron, aluminium, titanium and manganese bonded together. The bond is very weak in the freshly obtained material, but, on exposure, its strength increases at the same time as the characteristic hardening of the material. Laterite may have been formed by the weathering of basalts as in the Deccan of India, or of other rocks, such as gneiss, slate, sandstone and granite, as in Africa. It has been suggested that it may have been produced by the action of bacteria which precipitated silica in the colloidal form, the silica then being removed by dilute alkaline solutions formed at the same time. Laterite may also be regarded as a terrestrial silt, indistinguishable

¹ 'Memoirs of the Geological Survey. Special Reports on the Mineral Resources of Great Britain.' Vol. VI. *Refractory Materials: Ganister, etc.* (London, H.M. Stationery Office, 1918).

mineralogically from the silts deposited by water. *Bauxite* has a structure very similar to laterite; in it hydroxides of alumina predominate.

Other refractory materials, for example chromites and some magnesites, have a structure consisting of crystalline grains cemented together by a crypto-crystalline cement. Hydrous magnesium or iron silicates are of frequent occurrence.

(c) *Amorphous or Crystalline Grains without Cement*. Some ceramic materials occur in loose incoherent beds, without any cement to bind the grains together. Many clays, sands, decomposed quartzites and kieselguhr are of this type.

Most clays in the natural state are composed principally of finely-divided clay minerals and sand; some contain gravel and even boulders of stone embedded in the clay. Glacial drift detritus, in certain localities, is rich in limestone powder and is then not suitable for brick manufacture.

Much useful information on the composition of clays can often be obtained by mixing thoroughly a weighed quantity of the dried material with four or more times its weight of water and then passing the liquid suspension through a series of sieves of increasingly finer mesh. The residues on each sieve are washed free from finer particles, then dried and weighed to give their relative proportions. An examination of each with a hand lens or microscope will show that most of the particles of greater size than 0.005 in. consist almost entirely of sand.

Among the most important sands for refractory purposes is the *Dinas sand*—a pale-yellow material produced by the disintegration of the famous Dinas quartzite—occurring in the Vale of Neath, Glamorganshire. Several other silica sands are found in various geological formations, especially in the Lower Greensand and Estuarine beds.

Another important sand is that from Loch Aline; it is remarkably free from iron and is in great demand in the glass industry.

Dolomite sands are deposits formed by the weathering of dolomitic limestone; the calcareous material, being soluble in water containing carbon dioxide, is removed in solution, leaving the less soluble magnesium mineral behind, together with some silica sand. Such sands are seldom pure enough for use as refractory materials.

Chromite occasionally is found as a loose detrital sand, the beds of which tend to be variable.

Zirconia and *zircon* are commonly in the form of sands in river-beds and along the sea-shore. They are associated with other loose materials derived from pegmatites and syenites. *Monazite sands* are of a similar nature.

Many of the rarer refractory materials occur in individual grains disseminated through igneous rocks or in sand deposits and placers derived from the disintegration of such rocks. The principal of these are beryllium oxide, titanium oxide, zirconia, ceria, didymia, lanthana, thoria, yttria, etc.

(d) *Entirely Glassy Materials*. These are very uncommon in nature and can only be found in a rapidly cooled magma which is rich in silica, e.g. the mineral obsidian and basalts.

Massive Structures. Many ceramic materials occur in the form of large masses; these depend largely on the mode of formation. The principal types are as follows:

Stratified masses are those in which the materials are aggregated in the form of

layers, strata or laminations. This structure is characteristic of most of the rocks laid down by the action of water and includes the majority of clays, which have been carried in suspension in rivers and have finally settled at the bottom of rivers, lakes, seas, etc. They are in beds or strata of varying thickness and often interlaid with layers of sand and other materials. For further details see *British Clays, Shales and Sands*, by A. B. Searle (Griffin).

Unstratified masses are those in which the materials show no special arrangement or lines of stratification. This type of structure is common amongst raw ceramic materials and is also characteristic of many of the finished products. In fact, in the case of the finished articles, it is the most desirable structure.

The nature of unstratified rocks comes within the province of geology and is outside the scope of the present volume. It is of interest, however, that most residual clays and some sedimentary ones are unstratified, as are also some forms of silica rock, magnesite and zirconia. Unstratified materials may be (i) homogeneous or uniform, or (ii) heterogeneous or irregular in character and in the arrangement of the particles of which they are composed.

Homogeneous structures are those which are uniform throughout the whole mass and may therefore be expected to have the same physical properties, no matter from which part a sample may be taken. They differ from stratified, laminated and other heterogeneous structures in the absence of definite planes of cleavage or other signs of being composed of 'units' of different character.

In the manufacture of articles such as pottery and brick-shapes, homogeneity is usually of great importance and any definitely laminated or segregated type of structure must be destroyed during the process of manufacture.

As homogeneity is closely allied to 'texture' further information is given in Chapter VII.

Flaky and Laminated Materials. When a rock appears to be composed of very thin *flakes*, it is said to be *laminated* and if the splitting occurs along the same plane as the bed in which it was deposited the structure is termed *shaly*. If the material cleaves in any other direction than one parallel to the bedding plane, the term *fissile* is employed to distinguish such a rock from the *shales*. In some laminated clays, each layer is silty in its lower part and carrying the finest clay at the top; these bands are known as *varves* which, in some clays, have been shown to be annual layers.

Many clays and all shales show signs of stratification; they may generally be split into thin flakes and foliations parallel to the bedding plane. When a clay has been greatly compressed in a direction at a large angle to the bedding plane and simultaneously subjected to great heat, *slate* may be produced.

Flaky clays do not readily form a homogeneous plastic mass except after an excessive amount of grinding and are very difficult to use satisfactorily. The structure of a clay is of great importance industrially; a compact, laminated type is highly objectionable for it can seldom be completely destroyed and a mass of homogeneous structure produced except at a prohibitive cost. Two clays may have the same chemical composition, but one may be useless and the other valuable simply because of the differences in their structures. The best clays have a perfectly homogeneous texture and are free from any laminated structure; but, for various reasons, laminated clays are often used and with care can be made into satisfactory articles. It is,

however, essential to break them down to such an extent as to destroy all the laminations, otherwise the various laminae may not unite properly and the finished articles will be weak along the line of cleavage.

Lamination also occurs in some sandstones, ganister, bauxite, laterite, etc. Siliceous materials, other than clay, which show lamination should be avoided, as their structure is not easily destroyed in the course of making them into bricks, etc.

Sometimes a somewhat laminated structure is desirable, particularly in the case of graphite used for making crucibles and other shapes. The best graphites for this purpose consist of small flakes which adhere and form a laminated mass. Of American graphites, those from Alabama have the smallest and thinnest flakes; the flakes in Pennsylvanian graphites are slightly larger and thicker; whilst those from graphite from Canada are even larger and more irregular. The graphite from Madagascar consists of grains nearly twice as large as those in the American materials. Ceylon graphite is the most preferred; it has very thin rectangular or triangular grains, rather than true flakes; it is very satisfactory and gives most durable products, whilst articles made from a coarser and more obviously laminated structure tend to spall.

Foliated structures are produced by the recrystallisation of some of the constituents of a rock along lines parallel to the original bedding or along joints or cleavage planes, the rock being afterwards subject to lateral pressure. A foliated structure is characteristic of the schists but is not common in clays and other ceramic materials. Schistose quartz on account of its foliated nature is not satisfactory for making silica bricks, as those made from it tend to spall badly.

Cellular structures and substances are not common in clays. Of other ceramic materials the most important ones with a cellular structure are: (a) those such as pumice, which are too fusible to be used to any great extent as refractory materials, and (b) diatomaceous earths, which consist of the minute, siliceous skeletons of dead marine and freshwater plants and animals such as diatoms, radiolaria, etc. One of the most extensively used refractory materials with a cellular structure is kieselguhr. Its texture is readily seen when it is observed through a microscope, though to the naked eye it appears to be structureless. Moler consists of a similar material to kieselguhr but it is contaminated by considerable proportions of clay and often by volcanic ash. The clay acts as a bond which unites the other particles into a fairly strong mass.

A cellular structure in bricks and some other clay articles can be produced by mixing the raw material with sawdust, seeds or other organic matter. This burns away in the kiln, leaving a highly cellular and porous mass. The same effect can be achieved by introducing a gaseous component into the raw material (e.g. zinc and hydrochloric acid; calcium carbonate and acid) or by adding a foaming agent and heating air into the material.

Concretionary structures consist of a nucleus surrounded with layers of aggregations of other materials, the whole forming irregular masses and nodules. This kind of structure is often formed with nuclei of leaves, shells or the remains of plants and animals, which are deposited in water containing salts or silica in solution. Hämatite, limonite, clay ironstone and other forms of iron oxide commonly occur in nodular masses. Ironstone pebbles frequently show traces of a fossilised nucleus when

broken across. Limestone and some forms of silica are found as concretionary deposits, the former often resulting from extensive coral formations. Oolitic limestones are frequently, and dolomites more rarely, composed of concretionary masses. Flint occurs in nodular form frequently of large size associated with calcareous matter. Bauxite and laterite often occur in small round grains, varying in size from a pea to 1 in. in diameter and such nodules are sometimes separated from the matrix. Crypto-crystalline magnesite often forms nodular accretions.

Segregated structures are those in which part of the material forms veins or segregated masses in other rocks, such as vein-quartz, magnesite bands traversing masses of serpentine and hæmatite, spathic and magnetic iron ores occurring as large irregular masses in other rocks. Chromite frequently is present in massive and lenticular forms and as veins traversing serpentine and peridotite rocks and also in irregular masses in residual clays associated with serpentine.

Fibrous structures in ceramic materials are rare; the only one within the scope of this volume is asbestos. It has a fibrous structure, the crystalline grains forming long flexible fibres which interlock and produce a strong mass. Of the several varieties of asbestos, chrysotile is specially valued on account of the strength and length of its fibres.

Capillary structures are present in materials which behave as though they were composed of a multitude of minute tubes, each of which is of an extremely small diameter. In clays and clay products a capillary structure is somewhat analogous to cellular structure. It is best understood by observing the behaviour when the lower end of a very narrow tube is dipped into a liquid which wets it; the liquid rises in the tube to a greater height than that of the external liquid, because the surface film is in tension and the liquid in the tube gains in potential energy. The liquid rise will be greater with smaller-diameter tubes and will also depend on the tension or energy of the surface.

Porous clays and clay products contain an assemblage of small cellular units, many of which are connected through narrow necks; in this sense, they may be regarded as capillary structures.

A capillary structure has a great influence on the mechanism whereby water is taken up into a porous body, or lost from it during drying. This may be beautifully demonstrated by immersing such a body in a solution of a coloured compound allowing penetration on one face only; conversely, the migrational effect along capillaries is also brought out by drying such a body which has previously been impregnated with a coloured solution—the colour is concentrated in the outside areas.

The efflorescence which sometimes forms on bricks and other porous substances is due primarily to their capillary structure, which enables a solution of salts contained in the mass as a whole to become concentrated at the surface. When the solvent (water) evaporates, the salts are left as a 'deposit' on the surface of the article.

MUDS AND PASTES

MANY pastes which occur in nature are known as *muds*. They are often irregular in composition and of limited usefulness in their natural state.

Pastes are made artificially by mixing small particles of solid matter with one or more liquids, and whilst they have many characteristics of both solid and liquid substances, are merely physical mixtures and not chemical combinations, yet they have additional properties which cannot be fully predicted from those of their constituents. Thus, a sample of brick-dust may appear to have a physical structure very similar to that of the dry clay from which it is made, but if each material is separately mixed with about one-fifth of its weight of water, the clay will produce a paste which has very definite characteristics, such as plasticity, flow under pressure, etc., which the wet dust does not possess. If the clay paste is allowed to stand on a slightly-sloping board it will harden gradually as a result of the loss of water by evaporation, but wet brick-dust will allow a considerable portion of water to drain away, and the solid material, as it dries, will become increasingly friable and will, at a slight touch, fall to powder. In other words, in a true paste, there is much more cohesion between the solid and liquid particles. This cohesion varies with different liquids and solids; thus, clay readily forms a paste with water or oil, but not with paraffin or with alcohol.

The chief value of pastes in the clayworking and allied industries is the ease with which they can be moulded into convenient shapes, which they retain indefinitely.

In general, a satisfactory paste can be produced only when the solid constituent is in the form of a powder. Hence, indurated clays and massive pieces of material must usually be ground before they can be made into a paste.

Many clays occur in nature in a pasty form; the consistency of such clays can be varied by adding more water, the amount required depending upon the nature of the material and on the amount of water previously present in it. The larger the proportion of water, the more mobile will be the resultant paste.

SUSPENSIONS (SLURRIES AND SLIPS)

Suspensions of solid substances (chiefly in water) occur in nature in streams, rivers, lakes and seas and, less noticeably, when rain-water breaks down a material and carries away some of it in a runlet. Natural suspensions are of great importance as the means whereby large masses of clay, etc., have been sorted and transported to other areas, where—as the material settles out of the suspension—secondary deposits, such as most clays and sands of commercial value, are formed. Artificially-prepared suspensions are sometimes known as slips or slurries; a *slurry* is a suspension of a *crude* clay or other ceramic material, and a *slip* is one which has been more carefully prepared.

A *suspension*, *slip* or *slurry* is a mixture of solid and liquid in which the liquid phase predominates, so that the solid is suspended throughout the liquid. The properties of clay slips are dependent chiefly upon the colloidal state of the suspended matter in them, and, like pastes, are intermediate between solids and liquids. A slip, however, is more like the liquid extreme in that it takes the shape of the vessel in which it is contained. It also flows like a liquid and does not require any pressure to deform it, whilst a solid or a paste will not flow, but only changes its shape when subjected to pressure.

Slips are largely used in the manufacture of clay and other ceramic products by the process known as *casting* (see Chapter VIII). The surfaces of some wares are coated with clay, clayey mixtures, or glaze, which is applied in the form of a slip, the body being sufficiently porous to absorb the water and leave a thin coating of solid matter on the surface. The use of slips in this manner is often very convenient for applying cheaply and almost instantaneously a much thinner layer than would otherwise be practicable.

Although a slip consists of solid particles suspended in a liquid medium, it is not necessarily a permanent suspension. The grains may settle out, partially at least, if it is allowed to stand or is not continuously agitated. In this, slips are unlike *colloidal suspensions*.

A *colloidal suspension* is a mixture of solid and water, where the individual grains of the solid are very small and are permanently dispersed in the liquid medium. Although colloidal suspensions are sometimes regarded as intermediate between a solid and a liquid, they possess unique properties and are quite distinct from a simple mixture of solid particles and liquid. Thomas Graham, in 1861, discovered one of the chief characteristics of colloids when he found that certain liquids (apparently solutions of glue, gelatin, and similar substances) behaved quite differently from normal solutions (e.g. salt in water), inasmuch as the former would not pass through a membrane having water on the other side of it, whilst the latter passed through readily. To these non-permeating, apparently amorphous materials he applied the term colloid (from *kolla*, glue or gum) and supposed that they were a separate class of substances. Since the time of Graham, however, it has been found that most substances can be obtained in the colloidal state in the presence of a liquid in which they are insoluble.

A more detailed description of colloidal solutions and their properties will be found in Chapter VIII.

Many changes occur in the state of aggregation of ceramic materials as a result of exposure to the weather, volcanic action, percolating solutions and various earth movements. The study of these natural changes is chiefly the work of geologists and mineralogists and is largely outside the scope of this volume. During the manufacture of ceramic articles of various kinds the structure of the original material is generally destroyed, so that a rock with an unsuitable structure may not be harmful.

The alteration of the structure of the raw material is effected in various ways, such as (a) weathering, (b) crushing and grinding, and (c) calcining prior to making it into the desired shape.

Weathering consists of exposing the materials to the action of rain, snow, frost, etc., so as to break down the original structure of the clay or rock and render it easy to fashion into articles of various shapes. This method is commonly adopted in the case of soft, stratified materials such as clays, shales, etc. For harder and more resistant materials, which are not readily affected by the weather, this method is of little value and one of the other methods must usually be substituted.

Crushing and Grinding is employed to break down compact masses into smaller grains. Granular materials bonded by amorphous matter such as sandstones, clays, etc., are readily reduced to small grains, but with masses which are wholly crystalline

or consist of crystals in a glassy matrix, the grinding may be a very difficult and expensive operation.

Wholly crystalline quartzites need to be ground so fine before their structure is destroyed that the cost is often prohibitive, so that it is usually preferable to use a slightly less pure material which can be more easily reduced to a suitable state.

Materials of a shaly character sometimes cause difficulty by producing flat plates or flakes, which are undesirable in the finished goods.

Some clays are reduced to a *slip* by merely stirring them violently with water; this process is known as *blunging*.

Calcining consists in heating a material to redness or to a higher temperature, usually in order to decompose it partially. Such treatment is often useful in altering the structure of limestone, dolomite, magnesite, clay, flint and some quartzites, sandstones, etc. In some cases, such as the first four substances, the change in structure occurs through chemical dissociation, whilst in the last two substances changes in volume occur, so that strains are set up in the material, which cracks and can then be readily reduced by crushing to a structureless sand.

Clays and other ceramic materials are composed of primary and secondary minerals formed by geological processes and by them mixed together and compacted into masses of various types. The nature of these mineral components and the contribution they each make to the properties of the raw material are considered in the following chapters.

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CHAPTER II

ATOMIC AND CRYSTALLINE STRUCTURE

ALL ceramic materials are composed of various units, just as a wall is built of stones or bricks. These may be regular in shape (as are bricks), or amorphous as lumps of glass appear to be. Under a microscope, these units can frequently be identified as minerals (see p. 49) with a regularity of optical property which is not visible with the unaided eye. X-rays enable other structural details and the internal arrangement of atoms within these minerals to be ascertained. Indeed, prior to the discovery of X-rays by Röntgen in 1895 and their application by the Braggs and others to the study of the structure of various minerals, the nature of many substances in the solid state was largely a matter of conjecture: since that time, great advances have been made. Much information has been available for many years on crystalline substances and various theories concerning their nature have been published, but fundamental details of atomic and ionic structure have been ascertained only within the last decade and valuable additional knowledge is still being gained.

The importance of this recently acquired knowledge of the intrinsic structure of clays and other ceramic materials and their products is steadily being recognised by manufacturers and users of these substances. Already considerable developments in ceramic industries and processes have been brought about by applying such knowledge, and the scope of the subject is almost unlimited. The basic structure of minerals is now of value in relating the properties of a ceramic material to its essential nature, whereas formerly there was only a series of apparently unrelated subjects. An understanding of the chemistry and physics of substances depends very largely on an adequate knowledge and application of their crystal structures.¹

Some of the Ancient Greek philosophers had concluded that all material substances were composed of separate or discrete particles. This idea was further developed by Isaac Newton and John Dalton, the latter using the term *atom*² to represent these fundamental particles, which he imagined to be natural *units* too small to be further divided or decomposed. It was recognised that these units were not all identical, yet they represented the ultimate subdivision of matter and were the elementary units which take part in chemical reactions. They termed the complex units formed from two or more atoms *molecules* and defined a substance composed of atoms of one single type as an *element*. Their work showed that the combinations of these atoms of the elements are always in constant proportions and that the equivalent combining ratios form the basis of atomic weights.

As early as 1864, Newlands recognised that some elements are remarkably like others in some of their properties and established that a periodicity exists whereby,

¹ The fundamental conception of matter, in general, is too detailed and diverse a subject to be dealt with fully in the present volume. There are many books which treat of it to which the reader may refer if he so desires.

² The word *atom* means 'that which cannot be cut or divided'.

ABLE II—IA. TABLE OF PERIODIC CLASSIFICATION OF THE ELEMENTS
(Based on Mendeléeff's and later discoveries)

Period	Group 0		Group 1		Group 2		Group 3		Group 4		Group 5		Group 6		Group 7		Group 8
	a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b	
I			H ¹ 1 0														
II	He ² 4 0				Be ⁴ 9 1												
III	Ne ¹⁰ 20 2		Na ¹¹ 23 0		Mg ¹² 24 3		Al ¹³ 26 9		Si ¹⁴ 28 1		P ¹⁵ 31 0		S ¹⁶ 32 1		Cl ¹⁷ 35 5		
IVa	A ¹⁸ 39 9		K ¹⁹ 39 1														
IVb			Cu ²⁹ 63 5		Zn ³⁰ 65 4		Ga ³¹ 69 7		Ge ³² 72 6		As ³³ 74 9		Se ³⁴ 78 9		Br ³⁵ 79 9		Fe ³⁶ Co ³⁷ Ni ³⁸ 55 8 58 9 58 7
Va	Kr ³⁶ 83 7		Rb ³⁷ 85 5		Sr ³⁸ 87 6		Y ³⁹ 88 9		Zr ⁴⁰ 91 2		Nb ⁴¹ 92 9		Mo ⁴² 96 0		Mn ⁴³ 99		Ru ⁴⁴ Rh ⁴⁵ Pd ⁴⁶ 101 7 102 9 106 7
Vb																	
VIa	Xe ⁵⁴ 131 3		Cs ⁵⁵ 132 9		Ba ⁵⁶ 137 4		La ⁵⁷ 138 9		Ce ⁵⁸ 140 1								
Intermediate: Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu																	
VIIa																	
VIIb			Au ⁷⁹ 197 2		Hg ⁸⁰ 200 6		Tl ⁸¹ 204 4		Pb ⁸² 207 2		Bi ⁸³ 209 0		Po ⁸⁴ 210		At ⁸⁵ 211		Os ⁷⁶ Ir ⁷⁷ Pt ⁷⁸ 191 0 193 1 195 2
VIIa	Rn ⁸⁶ 222		Fr ⁸⁷ 223		Ra ⁸⁸ 226		Ac ⁸⁹ 227		Th ⁹⁰ 232 1		Pa ⁹¹ 231		U ⁹² 238 1		Np ⁹³ 237		Pu ⁹⁴ Am ⁹⁵ Cm ⁹⁶ 239 241 242

TABLE II—Ib. REVISED TABLE OF ATOMIC WEIGHTS
(*International Union*) 1956

<i>Element</i>	<i>Symbol</i>	<i>Atomic No.</i>	<i>Atomic Weight</i>	<i>Element</i>	<i>Symbol</i>	<i>Atomic No.</i>	<i>Atomic Weight</i>
Actinium	Ac	89	227	Neodymium	Nd	60	144.27
Aluminium	Al	13	26.97	Neon	Ne	10	20.183
Americium	Am	95	(241)	Neptunium	Np	93	237
Antimony	Sb	51	121.76	Nickel	Ni	28	58.69
Argon	A	18	39.944	Niobium	Nb	41	92.91
Arsenic	As	33	74.91	(Columbium)	(Cb)		
Astatine	At	85	(211)	Nitrogen	N	7	14.008
Barium	Ba	56	137.36	Osmium	Os	76	191.02
Beryllium	Be	4	9.13	Oxygen	O	8	16.0000
Bismuth	Bi	83	209.00	Palladium	Pd	46	106.7
Boron	B	5	10.82	Phosphorus	P	15	30.98
Bromine	Br	35	79.916	Platinum	Pt	78	195.23
Cadmium	Cd	48	112.41	Plutonium	Pu	94	(239)
Caesium	Cs	55	132.91	Polonium	Po	84	210
Calcium	Ca	20	40.08	Potassium	K	19	39.096
Carbon	C	6	12.010	Praseodymium	Pr	59	140.92
Cerium	Ce	58	140.13	Proactinium	Pa	91	231
Chlorine	Cl	17	35.457	Promethium	Pm	61	(147)
Chromium	Cr	24	52.01	Radium	Ra	88	226.05
Cobalt	Co	27	58.94	Radon (or			
Copper	Cu	29	63.54	Niton)	Rn	86	222.00
Curium	Cm	96	(242)	Rhenium	Re	75	186.31
Dysprosium	Dy	66	162.46	Rhodium	Rh	45	102.91
Erbium	Er	68	167.62	Rubidium	Rb	37	85.48
Europium	Eu	63	152.0	Ruthenium	Ru	44	101.7
Fluorine	F	9	19.00	Samarium	Sm	62	150.43
Francium	Fr	87	(223)	Scandium	Sc	21	45.10
Gadolinium	Gd	64	156.9	Selenium	Se	34	78.96
Gallium	Ga	31	69.72	Silicon	Si	14	28.06
Germanium	Ge	32	72.60	Silver	Ag	47	107.880
Gold	Au	79	197.2	Sodium	Na	11	22.997
Hafnium	Hf	72	178.6	Strontium	Sr	38	87.63
Helium	He	2	4.003	Sulphur	S	16	32.066
Holmium	Ho	67	164.94	Tantalum	Ta	73	180.88
Hydrogen	H	1	1.0080	Tellurium	Te	52	127.61
Indium	In	49	114.76	Terbium	Tb	65	159.2
Iodine	I	53	126.92	Thallium	Tl	81	204.39
Iridium	Ir	77	193.1	Thorium	Th	90	232.12
Iron	Fe	26	55.85	Thulium	Tm	69	169.4
Krypton	Kr	36	83.7	Tin	Sn	50	118.70
Lanthanum	La	57	138.92	Titanium	Ti	22	47.90
Lead	Pb	82	207.21	Tungsten	W	74	183.92
Lithium	Li	3	6.940	Uranium	U	92	238.07
Lutecium	Lu	71	174.99	Vanadium	V	23	50.95
Masurium (or				Xenon	Xe	54	131.3
(Technetium)	Ma	43	(99)	Ytterbium	Yb	70	173.04
Magnesium	Mg	12	24.32	Yttrium	Y	39	88.92
Manganese	Mn	25	54.93	Zinc	Zn	30	65.38
Mercury	Hg	80	200.61	Zirconium	Zr	40	91.22
Molybdenum	Mo	42	95.95				

when elements are arranged in order of their atomic weight, similarity occurs at every eighth one. Mendeléeff extended the idea and in 1869 published his Periodic Table (Table II.IA) which, with but little modification, is still in general use. When this Table was first outlined, many elements had not been discovered but were predicted. The complete series, recognised at the present time, is shown in Table II.IA. In this Table, the elements are arranged in horizontal series and vertical groups, in increasing order of the atomic weights. Like elements occur in the same vertical column, but some have to be further divided into sub-groups *a* and *b* for completeness. These subdivisions are to indicate that, whilst some elements must be allocated to a particular vertical column, they resemble others in the same column less than might be expected; thus copper, silver and gold in Group I are placed to the right of the other elements (lithium, sodium, potassium, rubidium, etc.), to show this distinction. For this reason, the horizontal series in Periods IV and V are in two distinct parts. The rare earth elements (Atomic Weights 59-71) are shown in a separate (Intermediate) section because of their similarity in property. The atomic weight and number of each element in alphabetical order is shown in Table II.IB.

The Periodic Table enables many known physical and chemical facts to be more clearly understood. It was shown, for example, that the periodicity of valency, atomic volumes and atomic heats can all be related to the position of the elements in the Table and certain other characteristic properties can be predicted.

It is remarkable that the atomic weight of most elements is very nearly a whole number and the idea of a simple unit as the basis of all atoms was suggested by Dalton, who regarded the atom of hydrogen as the fundamental unit of atomic weight. More than a century passed before Moseley showed that the wave-length of X-rays emitted by each element when bombarded with electrons, increases in a simple ratio with the *atomic number* of the atoms as arranged in the order in the Periodic Table; this discovery led to the conclusion that atoms themselves were composed of still smaller units.

Notwithstanding the great importance of the Periodic Table, it was very largely neglected by ceramic chemists until about 1901 when William Burton drew attention to its value and applied it to his researches on glazes in connection with 'Lancastrian Pottery'.¹ Since that time it has been increasingly used in the study of new bodies and glaze compositions.

THE STRUCTURE OF ATOMS

THE present view of the structure of atoms is the result of detailed studies of electrical discharges through gases. This led to the discovery of various types of radiation, such as cathode rays, positive or α -rays and X-rays, a fuller account of which can be found in many books on Modern Physics. It was proved that the atoms of all elements consist of *electrons*, or negatively-charged particles, revolving around a core or nucleus, which has a net positive charge. The nucleus of all atoms is composed of *protons*, each of which bears a positive charge, and *neutrons*, which have no charge.

Both protons and neutrons are, by definition, of unit mass and about 1,840 times

¹ Private communication from his associate, A. Lomax.

heavier than an electron. Hence the weight of an atom is largely determined by the number of particles in its nucleus.

The charge on the nucleus depends on the number of unit positive charges, or protons, which is equal to the atomic number of the element or atom. The total positive charge of the nuclear protons is exactly sufficient to neutralise the negative charges of the electrons. As each electron is of unit negative charge, it follows that there must be an equal number of electrons and protons in a particular atom.

Although the diameter of the nucleus of all atoms is very small, *circa* 10^{-13} cm., the size of the atom itself is much greater, being determined by the size of the orbits in which the electrons revolve.

The protons, neutrons and electrons of all atoms are identical in all respects and atoms differ only in the number of these ultimate particles which they contain. The simplest atom is that of hydrogen, which consists of a single proton with one electron revolving in an orbit around it. The proton is thus a hydrogen atom devoid of its electron and is thus synonymous with the free hydrogen ion or H^+ . Although the electron is an even smaller particle than the proton, the hydrogen atom is more than 10,000 times larger than the ion. The atom may thus be regarded, in a simple way, as an infinitesimally-sized planetary system, with electrons in place of planets and the nucleus in the position of the centrally-located sun.

The number of atoms in the gram-atomic weight¹ of each element is always constant. This is termed the *Avogadro Number* and has the value of 6.02×10^{23} ; it is represented by the symbol N . Consequently, if the nucleus of an atom were composed only of protons, the atomic weight should, in all cases, be equivalent to the number of protons it contains, i.e. Z , or, in other words, to the atomic number, because each proton is of unit mass and almost all of the mass of an atom is centred in the nucleus. In most cases, however, the atomic weight of an element is nearer $2Z$; this is because neutrons also occur in the nucleus of atoms and these uncharged particles of the same weight as protons are present in similar numbers. However, the number of neutrons present in a particular atom is not always constant and this gives rise to the concept of *isotopes* which may be defined as atoms of the same element, having the same atomic number, but with slightly different atomic weights.

All atoms therefore consist essentially of three types of particles:

(a) *Electrons*, which are particles of unit negative charge revolving around a nucleus. They are of very small mass, being only 9.1×10^{-28} gm., or $1/1838$ of the weight of a proton.

(b) *Protons*, which are confined to the nucleus. These are of unit positive charge, and of unit atomic weight or mass.

(c) *Neutrons*, which are also situated in the nucleus, but are electrically neutral; they are of similar mass to the proton.

These three kinds of particles may be regarded as the fundamental bricks in the framework of the structure of an atom.²

¹ The gram-atomic weight of an element is simply the atomic weight expressed in grams.

² Modern developments have indicated that atomic configuration is more complex, but this simple picture is sufficient for the present purpose.

Electrons are the important units which determine the nature of an atom and which take part in chemical reactions. The electrons revolve around the nucleus in definite orbits and the number of electrons in any atom is equivalent to the positive charge of the protons in the nucleus. The atomic number also represents the number of electrons present in the atom. Hydrogen, for example, with the atomic number of 1 has one orbital electron; helium with atomic number 2, has two electrons; and, so on, up to curium with an atomic number of 96 and ninety-six electrons.

A simple picture of the atom was suggested by Bohr, who visualised the electrons as separate or discrete particles moving in definite orbits and occupying certain spacial positions at any specified time.

With the development of the wave mechanical theory,¹ Bohr's suggestion has been shown to be untenable and the electron distribution is now based on a statistical wave representation. Schrodinger and others visualise the distribution around the nucleus as in the form of an electron cloud and equations have been derived to predict probable positions at a given time.

In all atoms, the electrons revolve around the nucleus in a series of specified orbits or 'shells' and the number in each separate orbit is limited. The states of the electrons in any atom are defined by four *quantum numbers* which are designated n , l , s , and j .

The *quantum number 'n'* refers to the number or order of the orbit in which a particular electron revolves. Wave mechanical theory predicts that electrons revolve round the nucleus in a series of orbits or shells. The number of electrons in any one orbit is limited and is given by the expression $2n^2$, where n represents the order of that shell. Thus in the first orbit there can be only two electrons; in the second orbit, eight; the third, eighteen; and so on. The first shell has its orbit nearest to the nucleus, the other shells are at ever-increasing distances from the centre. Each of these orbits is given a symbol: electrons in the innermost shell, where $n = 1$, are referred to as being in the *K* shell; those in the second as being in the *L* shell; those in the third, the *M* shell, etc.

The *second quantum number 'l'* expresses the orbital angular momentum or the 'degree of ellipticity' of the orbit. The value of l can range from 0 to $n-1$. Thus if an electron is in the *M* shell or where $n = 3$, then l can be 0, 1, or 2. In other words, the orbit can be spherical (when $l = 0$), elliptical if $l = 1$; and even more ellipsoidal when $l = 2$. Electrons in the *K* shell (when $n = 1$) can only have $l = 0$ and therefore they must all have spherical orbits. In general the ratio of the major to the minor axes of the ellipsoidal orbit increases as l increases. The electrons in any particular shell can therefore be divided into sub-shells, each with different orbits, and the number of electrons possible in each sub-group of quantum number l is given by the expression $2(2l + 1)$; thus when $l = 2$ the number of possible electrons in this orbit is 10; where $l = 1$, there are 6 electrons possible; and when $l = 0$, there cannot be more than 2 electrons. The *M* shell, which can contain a maximum of 18 electrons, will have these distributed throughout three different orbits with

¹ In 1924, de Broglie suggested that all atomic particles are associated with waves of a definite frequency. Bohr's conception of circular and elliptical orbits is now replaced by the appropriate wave-functions. The old ideas are still useful in that they provide a simple picture of the atom which can be understood by most readers.

2, 6, and 10 electrons in each orbit respectively; those in the first group revolve in a spherical orbit, those in the second revolve in an elliptical orbit and those in the third group revolve in an even greater ellipsoid.

The *third quantum number 's'* represents the angular momentum or spin of the electron about its own axis; *s* always has the value of $\frac{1}{2}$.

The *fourth quantum number 'j'* expresses the total angular momentum of a particular electron. In other words, it is the resultant of the orbital and spin moments, represented as vector quantities; it is equal to $l + s$.

Any further quantum numbers which need to be introduced are only extensions of those already described. Thus in a strong magnetic field an electron can develop a spin in either of two directions, the magnitudes of which can be represented by $\pm\frac{1}{2}$. This magnetic quantum number is designated *m* and its relation to the spin of the electron by *m_s*.

It is to be expected that the orbit of an electron is also subjected to magnetic influences in a strong field. The magnetic component of *l* is termed *m_l* and its value must lie between $+l$ and $-l$.

Hence, every electron in an atom, in a strong magnetic field can be described by five quantum numbers with definite values as follows:

$$\begin{aligned} n &\text{ of value } 1, 2, 3, \dots \text{ etc.} \\ l &\text{ of value } 0 \text{ to } n-1 \\ s &\text{ of value } \frac{1}{2} \\ m_s &\text{ of value } \pm\frac{1}{2} \\ m_l &\text{ of value } +l \text{ to } -l \end{aligned}$$

The possible number of electrons in any shell is limited by *Pauli's exclusion principle*, which states that 'no two electrons in the same atom can have an identical set of quantum numbers'. In other words, no two electrons can be in the same place at the same time and doing the same thing. Hence, for electrons in any shell a series of possible positions can be calculated. For example: where $n = 1$

	<i>l</i>	<i>m_l</i>	<i>m_s</i>
i.e. the K shell	0	0	$+\frac{1}{2}$
	0	0	$-\frac{1}{2}$

Only two different quantum representations are possible for the electrons in the K shell, because *l* and *m_l* have the value 0, and *m_s* can only be $+\frac{1}{2}$ or $-\frac{1}{2}$.

When $n = 2$ there are more possibilities

<i>l</i>	<i>m_l</i>	<i>m_s</i>
0	0	$+\frac{1}{2}$
0	0	$-\frac{1}{2}$
1	+1	$+\frac{1}{2}$
1	+1	$-\frac{1}{2}$
1	0	$+\frac{1}{2}$
1	0	$-\frac{1}{2}$
1	-1	$+\frac{1}{2}$
1	-1	$-\frac{1}{2}$

Thus there can be a total of eight electrons in the L shell, each with a different quantum representation. These two examples show why the number of electrons in each shell of quantum number n is equal to $2n^2$.

All electrons with $l = 0$ are termed s electrons; those with $l = 1$ are termed p electrons; those with $l = 2$, d electrons; and those with $l = 3$, f electrons. In any sub-shell, i.e. electrons of a certain l value, the number of electrons possible is $2(2l + 1)$, because m_l can be any integer between $+l$ and $-l$, and m_s can be $+\frac{1}{2}$ or $-\frac{1}{2}$. For example, if l is 2, m_l can have the values $+2, +1, 0, -1, -2$; i.e. $2l + 1$; each of these can have magnetic spins of $+\frac{1}{2}$ or $-\frac{1}{2}$; consequently, the number of possible electrons is $2(2l + 1)$.

Table II.II shows the maximum possible number of electrons in each of the K, L, M shells, assuming that the electrons fit successively into shells, commencing with the K shell, then the L shell, etc., filling first the sub-shell s , then p , then d and so on.

TABLE II—II. MAXIMUM NUMBER OF ELECTRONS IN FIRST THREE ELECTRON ORBITS

Symbol	<i>K</i> shell		<i>L</i> shell		<i>M</i> shell		
n	1		2	2	3	3	3
	0		0	1	0	1	2
m_l	0		0	3	0	3	5
m_s	2		2	2, 2, 2	2	2, 2, 2	2; 2, 2, 2, 2
$2(2l+1)$, i.e. total electrons in sub-shell	2		2	6	2	6	10
$2n^2$, i.e. total electrons in complete shell	2		8		18		
Nomenclature*	(1s) ²		(2s) ²	(2p) ⁶	(3s) ²	(3p) ⁶	(3d) ¹⁰

* The number of electrons in a particular sub-shell is indicated by the number of the orbit, followed by the sub-shell number and the electrons it contains as an index figure.

THE ARRANGEMENT OF ELECTRONS IN ATOMS

THE element with atomic number 1 is hydrogen; it has its single electron in the K shell, which is thus not fully filled or completed. The next element, helium (atomic number 2), has two electrons—both in the K shell which is now completed. As the number of orbital electrons is increased they must go into the L shell, filling first the $2s$ positions, then the six $2p$ positions, at which point the second shell is complete as in the inert gas, *neon*, with an atomic number of 10. Elements with higher atomic numbers must have some electrons in the M shell.

A new electron will usually enter the sub-shell in which it will be held most firmly and with the greatest stability. The K and L shells are orbits which are relatively close to the nucleus and so the order for the electrons to enter is as expected, $1s, 2s$, and $2p$. In the M shell, however, the distance from the nucleus is greater, and

so the attractive force on the electrons in this shell is less than in the two previous ones. The orbit of the $3d$ sub-shell is an elongated ellipsoid and this is apparently less stable than the spherical orbit of the $4s$ sub-shell of the N layer. Once the $3p$ sub-shell has been completed with the inert gas, *argon*, atoms of increasing atomic numbers, potassium, calcium, etc., have some electrons which enter the $4s$ sub-shell before the $3d$ orbit is filled. The irregularity is found, on an increased scale, in the N , O , P and Q shells.

Table II.III shows the electronic structure of most of the ninety-six elements.¹

Elements in which the last (outermost) shell but one is incomplete usually have characteristic properties, such as variable valency. They are called *transitional elements*, and are of great value to the ceramic industry because their compounds are often coloured.

The arrangement of electrons shown in Table II.III represents those in atoms in an isolated state. In practice these are not very common, in most cases the electrons exist in combination with one another or as ions. The inert gases, helium, neon, argon, krypton, xenon and radon, are exceptions in having atoms with orbital structures capable of a stable, independent existence. A study of the electronic arrangements within these atoms has thrown considerable light on the nature of bond formation between two or more atoms.

The electrons in the various shells of the inert gases are distributed as follows:

TABLE II—IV. THE ELECTRONIC STRUCTURES OF THE INERT GASES

Element	At. No.	K orbit 1s	L orbit 2s 2p		M orbit 3s 3p 3d			N orbit 4s 4p 4d 4f				O orbit 5s 5p 5d			P orbit 6s 6p	
Helium	2	2														
Neon	10	2	2	6												
Argon	18	2	2	6	2	6										
Krypton	36	2	2	6	2	6	10	2	6							
Xenon	54	2	2	6	2	6	10	2	6	10		2	6			
Radon	86	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6

Helium and neon represent the condition where the K shell in the former, and the K and L shell in the latter are completely filled. In the other inert gases the electron configuration has the s and p sub-shells of the outer orbit completed with eight electrons and no others in the corresponding d and f sub-shells. It might be expected that such arrangements would be very stable, and they are, in fact, so. In all other elements one or more sub-shells of an orbit are not completely filled; there is always a deficiency or excess of electrons.

Four different types of electron structures can be recognised, each with special features:

Group 1. Atoms with outer completed shells or sub-shells. This group contains the inert gases which have the s and p sub-shells of their outer orbits complete.

¹ Elements with a higher atomic number than 92 have, in the main, only been produced in microscopically small amounts as a result of radio-active processes. There is some difficulty in determining the arrangement of the electrons in the outermost orbits, for these are weakly held and easily lost. Ninety-six elements have now been identified and occupy the positions as shown in the Periodic Table (Table II.IA).

TABLE II—III. THE ELECTRONIC STRUCTURES OF THE ELEMENTS

<i>Symbol of Element</i>	<i>At. No.</i>	<i>K orbit 1s</i>	<i>L orbit 2s 2p</i>	<i>M orbit 3s 3p 3d</i>	<i>N orbit 4s 4p 4d 4f</i>	<i>O orbit 5s 5p 5d</i>	<i>P orbit 6s 6p 6d</i>	<i>Q orbit 7s</i>
H	1	1						
He	2	2						
Li	3	2	1					
Be	4	2	2					
B	5	2	2 1					
C	6	2	2 2					
N	7	2	2 3					
O	8	2	2 4					
F	9	2	2 5					
Ne	10	2	2 6					
Na	11	2	2 6	1				
Mg	12			2				
Al	13			2 1				
Si	14	Neon core of 10 electrons (1s) ² (2s) ² (2p) ⁶		2 2				
P	15			2 3				
S	16			2 4				
Cl	17			2 5				
A	18			2 6				
K	19	2	2 6	2 6	1			
Ca	20				2			
Sc	21				2 1			
Ti	22				2 2			
V	23	Argon core of 18 electrons (1s) ² (2s) ² (2p) ⁶ (3s) ² (3p) ⁶		3 2	2			
Cr	24			5 1	2			
Mn	25			5 2	2			
Fe	26			6 2	2			
Co	27			7 2	2			
Ni	28			8 2	2			
Cu	29	2	2 6	2 6 10	1			
Zn	30				2			
Ga	31				2 1			
Ge	32	Copper core of 28 electrons (1s) ² (2s) ² (2p) ⁶ (3s) ² (3p) ⁶ (3d) ¹⁰		2 2	2 2			
As	33			2 3	2 3			
Se	34			2 4	2 4			
Br	35			2 5	2 5			
Kr	36			2 6	2 6			
Rb	37	2	2 6	2 6 10	2 6	1		
Sr	38					2		
Y	39					2		
Zr	40					2		
Nb	41	Krypton core of 36 electrons (1s) ² (2s) ² (2p) ⁶ (3s) ² (3p) ⁶ (3d) ¹⁰ (4s) ² (4p) ⁶			1	1		
Mo	42				2	1		
Ma	43				4	1		
Ru	44				5	1		
Rh	45				6	1		
Pd	46				7	1		
					8			
					10			

TABLE II—III. THE ELECTRONIC STRUCTURES OF THE ELEMENTS

Symbol of Element	At. No.	K orbit 1s	L orbit 2s 2p	M orbit 3s 3p 3d	N orbit 4s 4p 4d 4f	O orbit 5s 5p 5d	P orbit 6s 6p 6d	Q orbit 7s
Ag	47	2	2 6	2 6 10	2 6 10	1		
Cd	48					2		
In	49					2 1		
Sn	50					2 2		
Sb	51					2 3		
Te	52	(1s) ² (2s) ² (2p) ⁶ (3s) ² (3p) ⁶ (3d) ¹⁰ (4s) ² (4p) ⁶ (4d) ¹⁰				2 4		
I	53					2 5		
Xe	54					2 6		
Cs	55	2	2 6	2 6 10	2 6 10	2 6	1	
Ba	56						2	
La	57						2	
							1	
Ce	58	2	2 6	2 6 10	2 6 10	2 6	1	2
Pr	59						1	2
Nd	60						1	2
Il	61						1	2
Sm	62						1	2
Eu	63						1	2
Gd	64						1	2
Tb	65						1	2
Dy	66						1	2
Ho	67						1	2
Er	68						1	2
Tu	69						1	2
Yb	70						1	2
Lu	71						1	2
Hf	72	2	2 6	2 6 10	2 6 10 14	2 6 2	2	
Ta	73					3	2	
W	74					4	2	
Re	75					5	2	
Os	76					6	2	
Ir	77					9		
Pt	78					9	1	
Au	79	2	2 6	2 6 10	2 6 10 14	2 6 10	1	
Hg	80						2	
Tl	81						2 1	
Pb	82						2 2	
Bi	83						2 3	
Po	84						2 4	
At	85						2 5	
Rn	86						2 6	
Fr	87	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6	1
Ra	88							2
Ac	89							2
Th	90							2
Pa	91							2
U	92							2

Group 2. Atoms with the outermost shell only partially filled. This group includes atoms with atomic number up to 17 (with helium and neon as exceptions), the sub-group elements in the Periodic Table and also the two elements which follow each inert gas in Table II.B, e.g. potassium and calcium following argon.

Group 3. Atoms with two outermost shells partially filled. This group includes the transition elements, the compounds of which are often coloured.

Group 4. Atoms with three outermost shells partially filled. This group includes the rare earth elements with an atomic number between 58 and 71. The *N*, *O*, and *P* shells are all incomplete. The element *lanthanum* (At. No. 57) has the electron arrangement shown in Table II.V.

TABLE II—V. THE ELECTRONIC STRUCTURE OF LANTHANUM

<i>K</i> orbit 1s	<i>L</i> orbit 2s 2p		<i>M</i> orbit 3s 3p 3d			<i>N</i> orbit 4s 4p 4d 4f			<i>O</i> orbit 5s 5p 5d			<i>P</i> orbit 6s 6p 6d	
2	2	6	2	6	10	2	6	10	2	6	1	2	

As the atomic number increases through cerium (At. No. 58), praseodymium (At. No. 59), etc., electrons fill the *4f* positions, the *5d* and *6s* shells remaining the same until the element hafnium (At. No. 72) is reached. This group is often termed the 'Lanthanide contraction' and the properties of all elements in it are similar. There is some evidence to suggest that there may be a similar contraction beginning with actinium (At. No. 89) in which the *5f* orbit is filled.

The Table of electron distributions can be related to the Periodic Table (p. 60). Elements which are alike in properties show remarkable similarity in the arrangement of the outermost electron orbits. The alkali elements illustrate this clearly, as shown in Table II.VI.

TABLE II—VI. THE ELECTRONIC STRUCTURES OF THE ALKALI ELEMENTS

<i>Element</i>	<i>At.</i> <i>No.</i>	<i>K</i> orbit 1s	<i>L</i> orbit 2s 2p		<i>M</i> orbit 3s 3p 3d			<i>N</i> orbit 4s 4p 4d 4f			<i>O</i> orbit 5s 5p 5d 5f			<i>P</i> orbit 6s 6p 6d		<i>Q</i> orbit 7s
Lithium	3	2	1													
Sodium	11	2	2 6	1												
Potassium	19	2	2 6	2 6	1											
Rubidium	37	2	2 6	2 6 10	2 6						1					
Caesium	55	2	2 6	2 6 10	2 6 10						2 6			1		
Francium	87	2	2 6	2 6 10	2 6 10 14						2 6 10			2 6		1

In all cases the outermost shell contains a single electron in the *s* orbit.

So general is the relation between properties and the distribution of electrons in the various shells that Thomsen and Bohr have been able to draw up another Periodic Table based on electronic structure in which like elements are joined by lines and the transitional elements are contained in frames (Table II.VII).

TABLE II—VII. THE PERIODIC TABLE
(Thomsen and Bohr)

																H 1																	He 2							
																Li 3	Be 4	B 5	C 6	N 7	O 8	F 9	Ne 10																	
																Na 11	Mg 12	Al 13	Si 14	P 15	S 16	Cl 17	Ar 18																	
K 19	Ca 20	<table> <tr> <td>Sc 21</td> <td>Ti 22</td> <td>V 23</td> <td>Cr 24</td> <td>Mn 25</td> <td>Fe 26</td> <td>Co 27</td> <td>Ni 28</td> </tr> </table>								Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36															
Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28																																	
Rb 37	Sr 38	<table> <tr> <td>Y 39</td> <td>Zr 40</td> <td>Nb 41</td> <td>Mo 42</td> <td>Ta 43</td> <td>Ru 44</td> <td>Rh 45</td> <td>Pd 46</td> </tr> </table>								Y 39	Zr 40	Nb 41	Mo 42	Ta 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54															
Y 39	Zr 40	Nb 41	Mo 42	Ta 43	Ru 44	Rh 45	Pd 46																																	
Cs 55	Ba 56	<table> <tr> <td>La 57</td> <td>Ce 58</td> <td>Pr 59</td> <td>...</td> <td>Yb 70</td> <td>Lu 71</td> <td>Hf 72</td> <td>Ta 73</td> <td>W 74</td> <td>Re 75</td> <td>Os 76</td> <td>Ir 77</td> <td>Pt 78</td> </tr> </table>								La 57	Ce 58	Pr 59	...	Yb 70	Lu 71	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86										
La 57	Ce 58	Pr 59	...	Yb 70	Lu 71	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78																												
Fr 87	Ra 88	Ac 89	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96																															

The important point established by this Table is, that if the atoms of an element have the same electron distribution in the outermost shells as the atoms of another element, then those two elements will have similar properties. The obvious implication is that many properties of an element are determined entirely by the arrangement of electrons in the outermost orbits of the atoms. The completed, internal shells are stable and, being disturbed only in exceptional circumstances, have less effect on the properties of the elements in which they are present.

ELECTRON BONDS BETWEEN ATOMS

THE manner in which electrons behave when they take part in reactions depends on the distribution of electrons in the orbits or shells. The atoms of the *inert gas* elements are very stable and unreactive, hence the electrons in these atoms must be in orbits which are complete in themselves and are not susceptible to change. Atoms of other elements appear to be constantly striving to change the distribution of electrons in their outermost shells to the arrangement found in the inert gas orbits, i.e. an external orbit ($s + p$) of 8. This can be brought about either by 'acquiring' or 'donating' some electrons. In general, an atom will 'take the easy way out'; if fewer

electrons have to be acquired than donated in order to form a distribution with completed orbits, then the electrons will be acquired and *vice versa*.

All the alkali atoms have one electron in their outermost orbit; they can form an inert gas shell either by donating one or by acquiring seven electrons; the first is 'easier' and invariably occurs.

When an atom has an excess or a deficiency of electrons it forms an *ion*. An *anion* or *negative ion* is an atom or group of atoms (radicals) which has gained one or more electrons and so contains an excess. A *cation* or *positive ion* is an atom or radical which has lost one or more electrons. Metallic atoms generally tend to lose electrons and become positively-charged cations; non-metallic atoms, like chlorine and bromine, usually acquire electrons and become negatively-charged anions. Some other atoms may acquire or donate electrons with almost equal ease and so can be either cations or anions in certain circumstances.

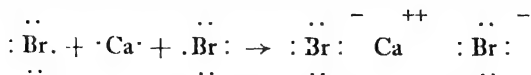
Cations may be uni-, di-, tri-, quadri-, etc., positively-charged, depending on the number of electrons they donate, e.g. Na^{1+} , Mg^{2+} , Al^{3+} , Si^{4+} , etc.¹ Negatively-charged anions may also have different charges depending on the number of electrons gained, e.g. Cl^{1-} , O^{2-} , N^{3-} , C^{4-} . The number of charges on the ion corresponds to the *valency*² or combining power of the atoms or elements. Atoms in the transitional group of elements are unusual in that they can transfer electrons from their outermost orbits to the subjacent *d* orbit of the previous shell. They have, therefore, variable valencies, so that iron, for example, may be Fe^{2+} , Fe^{3+} , or even Fe^{4+} .

Atoms will donate or acquire electrons when there is an available deficiency or surplus of electrons; this can occur if atoms capable of parting with electrons are brought into contact with other atoms requiring electrons to complete an inert gas shell.

In sodium atoms, the outer orbit, 3s, has one electron, whilst the *M* shell of chlorine atoms has seven. An atom of sodium can form the same stable distribution of electrons as in the inert gas, neon, by giving up one electron. An atom of chlorine can also acquire an inert gas shell (that of argon), by acquiring one electron. If a sodium atom donates its surplus electron to an atom of chlorine, two stable arrangements can result and the compound sodium chloride is formed in atomic proportions. Now the atoms are no longer electrically neutral; the sodium has lost an electron and has therefore a net positive charge whilst the chlorine atom has gained an electron and so is negatively charged. The reaction can be represented schematically by the notation suggested by Lewis:



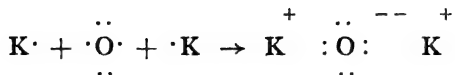
This consideration may be extended to more complicated cases, e.g. the formation of calcium bromide by the union of one calcium atom with two bromine atoms. The calcium atom gives up two electrons, one to each of two bromine atoms, thus:



¹ Occasionally, the + or - sign is repeated the necessary number of times, instead of preceding it by a number, e.g. Na^{++} , Mg^{+++} , Al^{++++} , Si^{++++} , etc.

² For further information on valency see most books on Physical Chemistry.

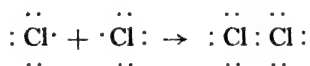
Potassium oxide illustrates the case where two atoms each donate one electron to another atom



This mechanism is termed **ionic bonding**, because the electrostatic charges of Coulomb attractive forces hold the two oppositely-charged ions together.

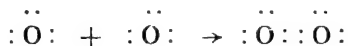
The product of the combination of atoms is called a *molecule*, which is the smallest quantity of a compound that can exist alone.

Another type of union of atoms which is very common, is known as the mechanism of *electron sharing* and of this the halogens provide a good example. The atoms of these elements have seven electrons in their outermost orbit. If two such atoms combine to share a pair of electrons then both of them will have effectively an inert gas configuration. Thus:



This is called **covalent bonding**; by it the atoms are held together by the shared electrons which are part of the orbits of all the atoms forming the molecule. The *shared electron pair* must have opposite spins to be in accordance with the Pauli Exclusion Rule (p. 65).

More than one pair of electrons can be shared. For example, an oxygen atom must share two pairs of electrons to form an oxygen molecule.



The union of atoms by either ionic or covalent bonds results in the formation of a stable molecule with the same distribution of electrons around each atom as there is in an inert gas. Molecules are capable of independent existence whereas single isolated atoms are found only in exceptional circumstances.

There are other types of bonding between atoms, two of which are described below: reference to a third and fourth (the hydrogen and hydroxyl bond) will be made later.

(i) **Van der Waal bonding.** When gases are cooled they liquefy and the atoms must therefore come together in some way. This also occurs in the inert gases, yet no electron transfer or sharing can result. The atoms exert some influence on one another but the mechanism is not fully understood. This type is termed *Van der Waal* bonding and is described more fully on p. 129.

(ii) **Metallic bonds.** There is another type of bonding between metal ions. Sodium atoms, for example, can unite with other similar atoms to form a strong bond, yet all the atoms are alike and each contains one electron in the outermost shell. It is conceived that each gives up an electron and becomes a positively-charged ion. The free electrons then wander about the structure without being attached to any particular ion. As a result, metals have characteristic properties such as conductivity, malleability, etc. (see p. 76).

THE BONDING OF ATOMS AND IONS IN SOLIDS

ATOMS may combine with others of similar or unlike type by one or other of the bonding mechanisms outlined in the previous section. In the simple examples which have been illustrated, the end product is a *molecule*, which is a complete and stable unit within itself. Such molecules have a definite existence in gases, liquids and in some kinds of solids and in these cases the individual particles of matter are distinct and separate and not strongly bonded to other particles in the immediate vicinity.

In crystals, however, there is a perfect continuum and X-ray analysis has shown that such substances cannot consist of discrete molecules placed either randomly or symmetrically but—except in isolated instances—of atoms, each of which is surrounded by a fixed number of other atoms, either of the same type or different. The linkages between all atoms are similar and there is no preferential bonding as would be the case if discrete molecules existed. Sodium chloride, for example, forms crystals in which each sodium atom or ion is centrally positioned with respect to six chlorine atoms, and each chlorine atom is symmetrically surrounded by six sodium atoms. The linkage between all atoms is identical throughout the crystal. Therefore, within the crystal lattice, the concept of simple electron transfer from a sodium atom to an adjacent chlorine is not tenable. The true picture is difficult to visualise unless the wave mechanical concept is introduced. The excess electron of a sodium atom must be imagined as a cloud with no discrete existence. Each chlorine atom shares a part (one-sixth) of this cloud and also acquires a further one-sixth share from each of five other sodium atoms in the immediate vicinity, so that six chlorine atoms each have a sixth share in the excess electrons of six sodium atoms. By this means, each atom acquires the same electronic structure as an inert gas and becomes an ion, the sodium ion being positively- and the chlorine ion negatively-charged. The resulting lattice is thus a three-dimensional network of positive and negative ions, and is called an *ionic crystal*, the bonds being between ions with opposite charges.

A crystal can also be formed by covalent bonds arranged in a similar fashion to ionic ones, the shared pair of electrons being distributed uniformly between all the adjacent atoms and forming *covalent crystals* with electrons, visualised only as a wave mechanical function, common to the orbits of several atoms.

Metallic crystals are simply groups of metallic ions with the excess electrons moving freely through the lattice; i.e. the extension of the metallic bond in three-dimensional space.

Crystals made up entirely of *Van der Waal linkages* are uncommon if they exist at all, but there are many examples of crystals in which they are associated with other kinds of bonds. Graphite, for example, is made up of sheets of covalently-bonded carbon atoms, the linkages between adjacent sheets being through Van der Waal linkages. In some clay minerals, the structures are held together by similar links. Bonds of this type are weak, and so both graphite and clay minerals can be sheared very easily because the sheets or plates glide readily upon each other. Van der Waal linkages appear to be due to the permanent dipoles which are set up in adjacent molecules. The attractive force is proportional to $1/r^n$ where n is usually about 6.

The four principal bonds which occur in molecules, namely ionic, covalent, Van der Waal and metallic, thus have their counterparts in crystalline structures. There are two other types of bonds, however, which occur in a limited number of lattices and involve many more atoms than there are in simple molecules. These are:

(a) **The Hydrogen Bond.** The atom of hydrogen is unique in consisting of a single proton and one electron. When hydrogen is incorporated in a crystal lattice it cannot be regarded as a separate atom with an electron configuration. It is better to regard the proton as a dimensionless centre of force which tends to modify the electronic structure of neighbouring atoms. For example, an oxygen ion (O^{2-}) can form a hydroxyl ion (OH^-) by combining with a hydrogen atom. The resulting ion is of similar size to the oxygen, but with only half its negative charge. In some structures hydrogen can form bonds which are almost ionic in character and in these cases the proton or H^+ acts as a kind of bridge. A hydroxyl (OH) unit, for example, can link with an adjacent oxygen ion. The hydrogen is represented as continuously jumping backwards and forwards between the two oxygens, although, in fact, a 'hybrid' structure is formed.



The resulting alternating or *resonance*¹ structure behaves as a rather weak bond, and is known as a *hydrogen bond*.

(b) **The Hydroxyl Bond.** When two or more hydroxyl (OH) groups occur close to each other in a crystal lattice, they may bond together by the electrostatic attraction between the negative and positive parts of the groups, thus:



Water molecules may also form similar bonds with suitable hydroxyl groups in a lattice.

When bonds of the hydrogen or hydroxyl type occur they usually do so along well-defined planes in a particular crystal. They are most common in minerals which are composed of sheets or planes of atoms and such bonds provide the linkages between adjacent layers. Bernal and Megaw² have discussed these two types of bonds in some detail and have given several examples which will be illustrated in Chapters III and IV.

There are thus six definite types of bonds which may be present in crystals, namely, ionic, covalent, Van der Waal, metallic, the hydrogen and the hydroxyl bond. All of these can occur in crystal lattices and more than one form of bond may be present in a single crystal though ionic and covalent bonds are by far the most common.

¹ A resonance structure is one where the atoms or electrons can occupy two or more alternative positions of similar energy values. The arrangement which results does not correspond to any extreme but has a higher bond energy and the distance between the atoms or groups involved is invariably shorter than when no resonance occurs. A typical example is graphite which is described in detail in Chapter IV (p. 178).

² Bernal, J. D., and Megaw, H. D., *Proc. Roy. Soc. (London)*, **A151**, 384, 1935.

TABLE II—VIII. PROPERTIES ASSOCIATED WITH
PRINCIPAL TYPES OF ATOMIC BONDS

(Modified and enlarged after Evans*)

<i>Property</i>	<i>Ionic Bond</i>	<i>Covalent Bond</i>	<i>Metallic Bond</i>	<i>Van der Waal Bond</i>	<i>Hydrogen and Hydroxyl Bonds</i>
Mechanical	Strong bonding hard crystals	Strong, hard crystals	Strength of varying degrees	Weak bonding soft crystals	Weak bonding. Slightly stronger
Thermal	Fairly high melting point. Low coefficient of expansion. When melted forms ions	High melting point. Low coefficient of expansion. Forms molecules in melt	Variable melting point. Long liquid-forming period	Low melting point. Large coefficient of expansion	Decomposed at fairly low temperatures
Electrical	Moderate insulation. When molten conducts by ionic transportation. Occasionally soluble in liquids of high dielectric constant	Insulators in both solid and liquid form	High conductivity by electron transport	Excellent insulators	Good insulators
Optical and magnetic	Behave like individual ions in adsorption and other properties. Similar in solution	High refractive index. Adsorption different in solutions and gaseous forms	Opaque. Similar properties in liquid state	Behave as individual molecules. Similar in solution and as gas	Show cleavage and usually have a dipole
Heat transfer	Fairly high insulation. Often conductivity increases with temperature	Highly insulating at all temperatures	Conductivity usually high	Good insulation properties	Good insulators
Structural	Non-directed structures of high co-ordination	Spacially directed and numerically limited. Structures of low co-ordination and low density	Non-directed structures of very high co-ordination. High density	Formally analogous to metallic bond. Usually high spacings	Weak bonds. Lines of easy fracture

* Evans, R. C., *An Introduction to Crystal Chemistry* (Cambridge University Press, London, 1939).

The various types of bond confer certain properties on crystals which are summarised in Table II.VIII.

The actual bonding between atoms in crystal structures is not well-defined and though the principal types are ionic and covalent linkages, most bonds are non-ideal and appear to be intermediate between the two kinds. The most direct proof of the composite ionic-covalent nature of some bonds is in the dipole moment of that linkage. In a true covalent bond, each atom must be non-polar, that is, each component atom is electrically neutral. On the other hand an ionic bond is polar because each atom acquires a charge; the donating-electron atoms become positive ions, or cations, whilst those receiving electrons become negative ions, or anions. A dipole¹ is thus set up between the two ions of ionic linkages but not when the bond is covalent. Most crystals exhibit dipole moments intermediate between the two extremes of ionic and covalent bonds.

With elements lying between the alkali metals and the halogens in the Periodic Table (p. 60), ionic bonding tends to give way to covalent and most positive ions have seldom lost more than three electrons or negative ions gained more than two. Thus, although Al loses three electrons to form Al^{3+} with a symmetrical and inert-gas electron-structure, its tendency to do so is strongly opposed by the attraction of the highly-positive ion so formed for electrons in the shells of surrounding negative ions.

The transition from a covalent to an ionic bond can be regarded as a displacement of the shared electron pair or pairs towards the more electronegative atom. Alternatively, a partly covalent bond can be imagined as one in which the electrostatic fields of two oppositely-charged ions (forming an ionic linkage) have been partially neutralised by the displacement of the transferred electrons to the positive ion.

Further evidence for mixed bond formation can be gathered from X-ray studies of bond angles and length. Composite bonds of other types of linkages are also recognised.

The degree of covalency, or alternatively the ionic character of a bond, has been calculated empirically by Pauling;² it is related to the relative *electronegativity* of the atoms forming that bond. The electronegativity of one atom with respect to another is derived from the 'electrochemical series' or list of electrode potentials. The alkali metals are the most highly electropositive, whilst the halogens are most electronegative. When elements with the greatest possible difference in electronegativity combine together the most ionic linkages will be formed. The electronegativity can be defined as the attraction of a neutral atom in a molecule for electrons. Pauling has compiled a list of values for most elements, some of which are shown in Table II.IX.

¹ An electrostatic field is set up between two ions of opposite charge, in like manner to the magnetic field between opposite poles of a bar magnet. The strength and intensity of this field is expressed as a *dipole moment*. Use has been made of dipole moments to find the relative orientations of bonds in molecules and crystals. If the moments of the individual bonds are known, the angles between the polar bonds can be calculated.

² Pauling, L., *The Nature of the Chemical Bond* (Cornell Univ. Press and Oxford Univ. Press, 1940).

TABLE II—IX. ELECTRONEGATIVITY OF THE ELEMENTS
(after Pauling)

			H 2.1				
Li	Be	B	C	N	O	F	
1.0	1.5	2.0	2.5	3.0	3.5	4.0	
Na	Mg	Al	Si	P	S	Cl	
0.9	1.2	1.5	1.8	2.1	2.5	3.0	
K	Ca	Sc	Ti	Ge	As	Se	Br
0.8	1.0	1.3	1.6	1.8	2.0	2.4	2.8
Rb	Sr	Y	Zr	Sn	Sb	Te	I
0.8	1.0	1.3	1.6	1.7	1.8	2.1	2.5
Cs	Ba						
0.7	0.9						

PERCENTAGE IONIC CHARACTER OF BONDS

PAULING has also evaluated the approximate percentage of ionic bonding between two atoms from the difference in electronegativity between them. The values are obtained from the dipole moments and the lengths of the bonds (from the absorption spectra) and taking the value of a completely ionised compound as 100. These are shown in Table II.X.

TABLE II—X. PERCENTAGES OF IONIC CHARACTER
OF BONDS

	% ionic		% ionic		% ionic
Mg—O	71	Si—O	50	Al—O	63
Mg—F	82	Si—Cl	30	Al—F	79
Mg—Cl	59	Si—Br	20	Al—Br	35

The difference in electronegativity can be calculated from Table II.IX and then this value used in Fig. II.1 to calculate the percentage ionic character of the bonding as in Table II.X.

It is difficult to visualise these intermediate types of bonds; the composition of the linkage can be represented only as a wave mechanical function and by postulating the occurrence of resonance between the two types of bonds.

THE SIZES OF ATOMS AND IONS

THE mass of an *atom* is nearly all centred on the nucleus, but the size of the atom depends on the extent of the electron orbits. X-ray diffraction methods have enabled the size of atoms to be measured with great precision.

Although the sizes of atoms can be calculated, their shapes are difficult to assess. The outermost orbits of electrons are often elliptical (see p. 64) and so, at any one instant, an atom may have an irregular shape. The electron field is dynamic, however, and the volume that it sweeps out in space as it rotates will be approximately

spherical, provided that the encircling, external electrical field is of uniform distribution. It is customary, although not always strictly correct, to assume that atoms (and ions) behave as spheres and their dimensions are expressed in terms of their diameters or radii. The size of an atom is defined as one-half the distance of closest approach between two adjacent atoms.

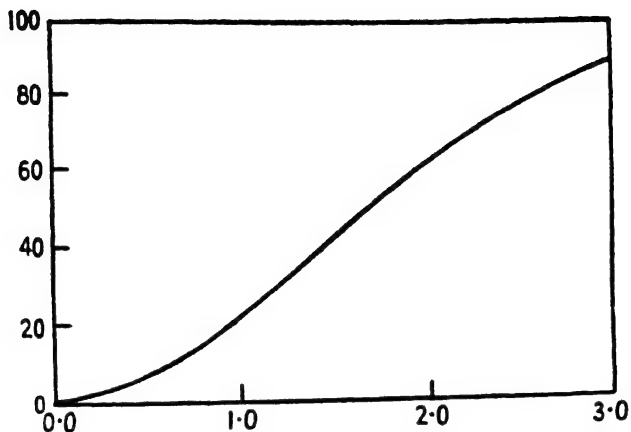


FIG. II.1. THE IONIC NATURE OF THE BOND AS A FUNCTION OF THE DIFFERENCE IN ELECTRONEGATIVITY OF THE ATOMS (after Pauling)

Fig. II.2 shows a graph of the atomic number against atomic radii. A succession of peaks occurs with the alkali elements in zenithal positions. The periodicity of these peaks is most marked and follows closely the curves of specific heat, valency, and other properties of atoms plotted against the atomic number.

The sizes of ions are of greater importance in the investigation of crystal structure because, in crystals, ions are the more common units. The measurement of the size of ions is fraught with difficulty for the ionic dimension varies with the environment. The sizes of ions have been measured by assuming that they behave as rigid spheres when in contact with one another. A series of analogous structures must be examined and the relative sizes can then be assessed.

There are great differences between the sizes of atoms and the sizes of ions of the same element. The positive ion is always smaller than the neutral atom of the same element, whilst a negative ion is larger than the corresponding neutral atom. The greater the positive charge of an ion, the smaller will be its size, all else being equal. This decrease in ionic radius with increasing nuclear charge is clearly shown by studying the series Na^+ to S^{6+} in Table II.XI. The electronic structure is the same in all cases.

In a crystal lattice a positive ion is surrounded by a number of negative ions, the number depending on certain factors which are discussed later in this chapter. The size of the internally-contained cation varies with the number of anions surrounding it, so that great difficulty is involved in measuring the size of ions under standard

conditions. This has, however, been largely overcome by Evans, and his results form the basis of Table II.XI. In all cases his values of ionic radii are based on the assumption that the ion is surrounded by six oppositely-charged ones; this may not be the stable state of some ions, but it does, at least, form a comparative basis.

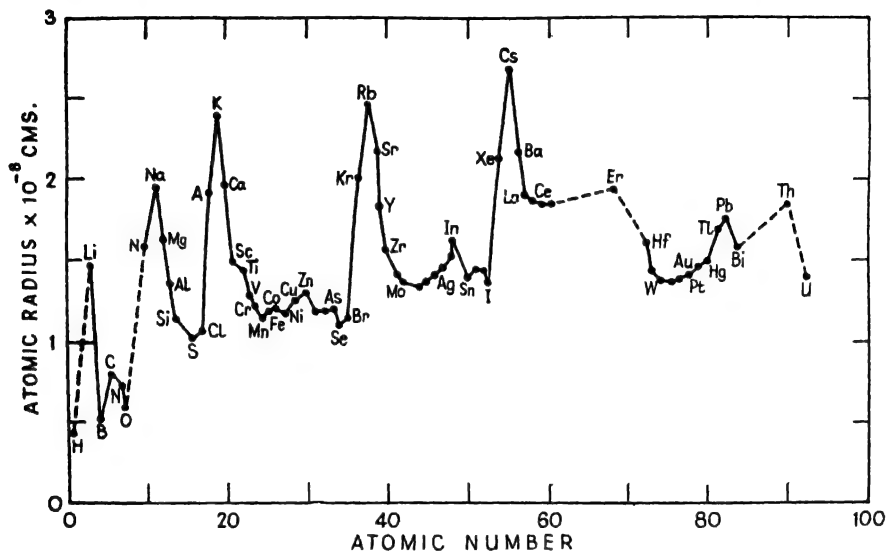


FIG. II.2. THE RELATIONSHIP BETWEEN THE ATOMIC NUMBER AND THE ATOMIC RADII OF ATOMS

THE ARRANGEMENT OF IONS IN A CRYSTAL LATTICE

A CRYSTAL lattice is composed of a large number of atoms or ions. A stable structure can be produced only if these ions are packed tightly and are retained in more or less rigid positions in space by surrounding units. Most inorganic crystals contain some proportion of ionic bonding in their atomic linkages. Therefore, the crystal lattice may be regarded as being composed of a series of positively- and negatively-charged ions. The anions are much larger than the cations (see Table II.XI) and, as would be expected, they play a larger part in determining the nature of the lattice. The cations, however, are instrumental in fixing the position which the anions can take up in space and, before the disposition of the anions can be considered, the cation-anion relationship must be established.

(1) THE PACKING OF CATIONS WITHIN ANIONS

In order to produce a stable arrangement the ions must be packed as closely as possible. Hence, the large anions must be situated in such a way as to enclose the smaller cations tightly. The manner in which this is brought about depends almost entirely on the relative sizes of the cations and anions. If it is assumed that ions

TABLE II—XI. IONIC RADII IN ÅNGSTROM UNITS ($1\text{Å} = 1 \times 10^{-8}\text{ cm.}$)
(after Evans)*Ions with Inert Gas Structures*

Valency	-3	-2	-1	+1	+2	+3	+4	+5	+6
			H 1.54	Li 0.78	Be 0.34	B 0.22			
N 1.80	O 1.32	F 1.33	Na 0.98	Mg 0.78	Al 0.57	Si 0.39	P 0.35	S 0.34	
P 2.01	S 1.74	Cl 1.81	K 1.33	Ca 1.06	Sc 0.83	Ti 0.69	V 0.4	Cr 0.35	
As 2.18	Se 1.91	Br 1.96	Rb 1.49	Sr 1.27	Y 1.06	Zr 0.87	Nb 0.75	Mo 0.68	
Sb 2.36	Te 2.11	I 2.20	Cs 1.65	Ba 1.43	La 1.22	Ce 1.18	Ta 0.68	W 0.68	

Ions of Sub-group Elements

Valency	+1	+2	+3	+4	+5
	Cu 0.96	Zn 0.83	Ga 0.62	Ge 0.44	As 0.4
	Ag 1.13	Cd 1.03	In 0.92	Sn 0.74	Sb 0.90
	Au 1.37	Hg 1.12	Tl 1.05	Pb 0.84	Bi 0.73

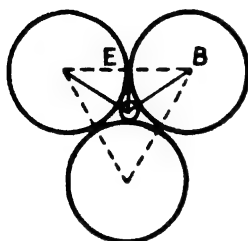
Ions of Transitional Group Elements

Valency	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
+2					0.91	0.83	0.82	0.78
+3	0.83	0.69	0.65	0.64	0.70	0.67		
+4		0.64	0.61		0.52			
+5			0.4					
+6				0.35				

behave as solid, rigid spheres, large-sized anions can be arranged in numerous ways to enclose smaller cations in the vacant spaces between them. The size of the enclosed cation determines the situations of the anions which surround it, because these must be so positioned as to hold the cation tightly; in fact they must touch it in as many points as possible.

Case (i) When three large spheres (anions) are arranged so that they each touch the other two, their centres are at the corners of an equilateral triangle. A smaller sphere (cation) can fit into the space between the three larger spheres. (Fig. II.3.)

If R is the radius (BE) of the larger spheres, the radius r of the smaller internal sphere can be calculated. BO is equal to $R + r$ and



$$\cos 30^\circ = \frac{BE}{BO} = \frac{R}{R + r} = \frac{\sqrt{3}}{2}$$

$$\text{Therefore } r = \frac{(2 - \sqrt{3})R}{\sqrt{3}} = 0.155R$$

FIG. II.3. THREE-FOLD OR EQUILATERAL CO-ORDINATION

Thus a sphere of $0.155R$ can fit between three others of radius R , when these are arranged so that their centres form an equilateral triangle.

Case (ii) For four anions to surround a central cation, the larger spheres must be arranged in the form of a regular tetrahedron.¹ Three of the spheres have their centres at the corners of the triangular base and the fourth rests at the apex, centrally above the other three, touching all of them. The small cation lies in the vacant space inside and must touch all the four anions.

The size of the central small sphere can be calculated quite simply, for the angle at the centre of a tetrahedron, i.e. $\angle AOC$ is $109^\circ 28'$. (Fig. II.4.)

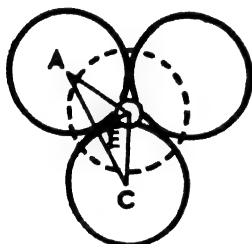


FIG. II.4. FOUR-FOLD OR TETRAHEDRAL CO-ORDINATION

Therefore

$\angle CAO = 35^\circ 16'$ for AOC is an isosceles triangle

$$\cos \angle CAO = \frac{AE}{AO} = \frac{R}{R + r} = 0.8166$$

$$\therefore R = 0.8166R + 0.8166r$$

$$r = \frac{0.1834}{0.8166} R = 0.225R$$

Thus a sphere of $0.225R$ can be surrounded by four spheres of radius R , situated at the corners of a regular tetrahedron.

Case (iii) Six large spheres can surround a centrally-placed smaller sphere when each is at the corner of a regular octahedron. Four of the large spheres are on the same plane, one other lies centrally above and the other centrally below the other four as shown in Fig. II.5, in which $BC = 2R$ and $AB = 2R + 2r$.

¹ A tetrahedron has three equilateral triangular sides and a base of the same shape; it is sometimes described as a three-sided or triangular pyramid.

$$\cos \angle ABC = \cos 45^\circ = \frac{BC}{AB} = \frac{2R}{2R + 2r} = \frac{1}{\sqrt{2}}$$

$$2\sqrt{2}R = 2R + 2r$$

$$r = (\sqrt{2} - 1)R$$

$$= 0.414R$$

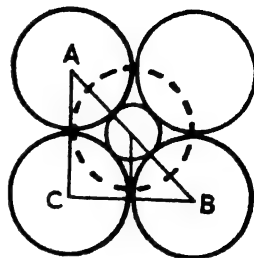


FIG. II.5. SIX-FOLD OR OCTAHEDRAL CO-ORDINATION

Therefore the largest cation which will fit in the centre of six anions arranged in the form of a regular octahedron is $0.414R$ where R is the radius of the anion.

Case (iv) When eight spheres surround a smaller one they occupy the corners of a cube. This is shown in Fig. II.6, where three of the front spheres A, B, C, and one back one G, are shown with the central smaller sphere.

The radius of the central sphere can be found from the two triangles ABC and ACG, in which $AC = CB = 2R$.

In the triangle ABC, $AB^2 = AC^2 + CB^2 = 4R^2 + 4R^2 = 8R^2$. AB is the face-diagonal of the cube and so also is AG, which must also equal $\sqrt{8R^2}$.

$$\begin{aligned} \text{In the triangle ACG, } GC^2 &= AC^2 + AG^2 \\ &= 4R^2 + 8R^2 = 12R^2 \\ \therefore GC &= \sqrt{12}R \end{aligned}$$

GC is a body-diagonal of the cube and passes from the centre of sphere C, through the diameter of the small sphere, to the centre of sphere G.

Therefore $CG = 2R + 2r$ (where r is the radius of the small central sphere)

$$2r = \sqrt{12}R - 2R$$

$$r = \sqrt{3}R - R$$

$$= 0.732R$$

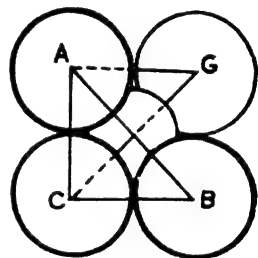


FIG. II.6. EIGHT-FOLD OR CUBIC CO-ORDINATION

Therefore, the largest size for a cation at the centre of eight anions (each of radius R), arranged at the corners of a cube, is $0.732R$.

The number of oppositely-charged ions which surround a central one is called the *co-ordination number* of that ion and the value is governed entirely by the relative sizes of the ions as shown in Table II.XII.

In deducing the foregoing figures it has been necessary to assume that all ions behave as rigid, perfect spheres, and remain so even when in contact with other unlike ions. This is not entirely correct, but as a guide to a visual picture of crystal structure, it can be regarded as approximately so. In actual fact, there is no rigid boundary to an ion comprising a nucleus and orbital electrons because when two ions approach each other, a repulsive force develops with great abruptness. This arises mainly as a result of the close approach of electrons in the outermost shells, and

hence the interatomic distance is limited; but, for most purposes, the ions in a crystal may be regarded as rigid spheres in contact and a characteristic radius ascribed to each ion.

TABLE II—XII. DEPENDENCE OF THE CO-ORDINATION NUMBER ON THE CATION/ANION SIZE RATIO

<i>Co-ordination Number</i>	<i>Dispositions of ions around central one</i>	<i>Critical radius ratio (cation/anion)</i>
8	Corners of a cube	1.000–0.732
6	Corners of a regular octahedron	0.732–0.414
4	Corners of a regular tetrahedron	0.414–0.225
3	Corners of an equilateral triangle	0.225–0.155
2	Linear	0.155–0

In the majority of structures which are of importance to ceramics, the predominating anions are those of oxygen. They surround various cations each of which is of a different size. The co-ordination number of these cations with respect to oxygen is of paramount importance in the crystal structure of all minerals.

If the radius of oxygen is taken as 1.32 Å, a series of cation/anion ratios can be calculated and hence the theoretical co-ordination of that cation with respect to oxygen. (Table II.XIII.)

TABLE II—XIII. THE CO-ORDINATION NUMBERS OF SOME CATIONS WITH OXYGEN ANIONS

<i>Ion</i>	<i>Radius</i>	<i>Cation/anion ratio</i>	<i>Predicted co-ordination</i>	<i>Observed co-ordination</i>
B ³⁺	0.22	0.16	3	3 (4)
Be ²⁺	0.34	0.25	4	4
Si ⁴⁺	0.39	0.30	4	4
Al ³⁺	0.57	0.43	(4) or 6	4 (5) 6
Fe ³⁺	0.67	0.51	(4) or 6	4, 6
Ti ⁴⁺	0.69	0.52	(4) or 6	4, 6
Mg ²⁺	0.78	0.58	6	6
Fe ²⁺	0.83	0.63	6	6
Zr ⁴⁺	0.87	0.66	6	6 (8)
Na ⁺	0.98	0.74	8	6 (8)
Ca ²⁺	1.06	0.75	8	6 (7) 8 (9)
K ⁺	1.33	1.00	8	(6), (7), 8 (9), (10) 12

The bracketed figures are co-ordination values which are not of common occurrence. The ionic radius varies with the co-ordination number and should be corrected. According to A. F. Wells, the ionic ratios can be calculated from Born's equation which can be rearranged to read:

$$\frac{r_p}{r_m} = \left(\frac{p}{m} \right)^{\frac{1}{n-1}}$$

where r_p and r_m are the radii of cations for co-ordination numbers of p and m respectively; n is approximately equal to 9.

Thus, when the co-ordination number changes from 6 to 8 the radius is increased by 1.036 times, and reducing the co-ordination number from 6 to 4 changes the size by a factor of 0.950.

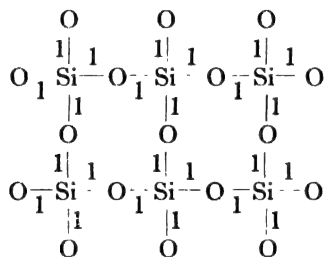
The principle stated above, that the co-ordination number is a function of the cation/anion size, forms the basis of *Pauling's first rule* of crystal structure.¹

The *second rule of Pauling* states that the sum of positive and negative charges in a lattice must be equal if the structure is to be stable. Therefore the valency residing on a particular cation must be divided equally amongst the co-ordinating anions. An anion consequently receives from each cation with which it is in contact a contribution towards the satisfaction of its own valency.

This may be illustrated by examples:

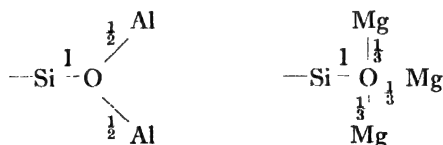
(i) Silicon is quadrivalent, i.e. Si^{4+} ; it is also in four-fold co-ordination with oxygen ions (O^{2-}). Hence, an ion of silicon contributes one valency share to each of four oxygen ions.

As each oxygen ion requires two valency units to become completely satisfied electrically, each must be in contact with two silicon ions to form a structure which is balanced electrically. This may be represented schematically as follows:



(ii) Aluminium is trivalent (Al^{3+}) and is in six-fold co-ordination with oxygen, so each oxygen ion receives only a half valency share from the aluminium ion. Each oxygen must, therefore, be in contact with, and receive a half valency share from, each of four aluminium ions.

(iii) In mixed structures, such as silicon and aluminium ions, with oxygen, the rule still holds and the valency of the oxygen must be satisfied by contributions from both silicon and aluminium ions, e.g.



Bragg² has suggested that lines of force may be imagined as starting on each cation and ending on each anion surrounding it. The valency of the cation divided

¹ Pauling, L., *Journ. Amer. Chem. Soc.*, 51, 1010, 1929.

² Bragg, W. L., *The Crystalline State* (Bell, 1933).

by its co-ordination number provides a measure of the strength of the electrostatic bond developed between the two ions. Table II.XIV shows the values for some of the important cations.

TABLE II—XIV. STRENGTH OF BOND IN CATION-OXYGEN LINKAGES

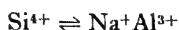
Cation	B ³⁺	Be ²⁺	Si ⁴⁺	Al ³⁺	Fe ³⁺	Ti ⁴⁺
Co-ordination No.	3	4	4	4, 6	6	4, 6
Strength of Bond	1	$\frac{1}{2}$	1	$\frac{2}{3}, \frac{1}{3}$	$\frac{1}{2}$	$1, \frac{2}{3}$
Cation	Mg ²⁺	Zr ⁴⁺	Fe ²⁺	Na ⁺	Ca ²⁺	K ⁺
Co-ordination No.	6	6, 8	6	6, 8	8	8, 12
Strength of Bond	$\frac{1}{3}$	$\frac{2}{3}, \frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{6}, \frac{1}{3}$	$\frac{1}{4}$	$\frac{1}{8}, \frac{1}{12}$

The co-ordination number depends on the cation to anion size ratio only when the bonding between the atoms is essentially ionic, because only in such circumstances can the individual units be regarded as independent spheres. In groupings of atoms where the bonding is principally covalent, the co-ordination number is decided by the number of covalent bonds formed by the atom and this favours small values. In most silicate structures, the bonding is sufficiently ionic for the units to be regarded as isolated spheres.

Isomorphous Substitution in Minerals. Only on very rare occasions can minerals be regarded as simple chemical compounds. Very frequently one or more ions are replaced in some proportion by other ions. The main replacements occur in the cation component; dolomite (magnesian limestone), for example, is similar to calcite, but with some of the magnesium ions exchanged for calcium ones. This form of replacement of one ion by another in a crystal lattice is termed *isomorphous substitution*.

Although the substitution in some minerals is apparently bewildering, the amount and type is limited in accordance with the principles laid down in the two rules of Pauling (p. 85). The replacing ion must be comparable in size to the original one or else the co-ordination may be different. Even then a suitably-sized ion may not be capable of replacement because its valency contribution is not the same; if this were so, then the electrical balance in the lattice would be destroyed. Typical replacements of common occurrence are: magnesium for calcium (when the co-ordination of the latter is 6); ferric iron for aluminium; ferrous iron for magnesium.

There are other instances where an ion of lower valency can replace one of a higher valency. When this occurs, additional ions have to be introduced into vacant spaces in the lattice. For example, aluminium (Al³⁺) can replace silicon (Si⁴⁺) for they are of comparable size, but a unit of valency has to be made up. In the feldspars, when a silicon ion is replaced by aluminium, a sodium or potassium ion is introduced to balance the valency. The substitution may be expressed as:



The substitutions $\text{Na}^+ \text{Si}^{4+} \rightleftharpoons \text{Ca}^{2+} \text{Al}^{3+}$ and $\text{Mg}^{2+} \text{Si}^{4+} \rightleftharpoons \text{Al}^{3+} \text{Al}^{3+}$ are also common.

Complex Ions. Acid radicles, such as CO_3^{2-} and SO_4^{2-} , are similar to co-ordinated groups in having the oxygen ions regularly arranged round the central cation. The linking, however, is mainly covalent and the atoms do not behave as rigid spheres. The outer electron orbits of the atoms merge together and as a consequence, the effective diameter is less than in electrostatic or ionic bonding. The geometrical arrangements of some of these complex units have been deduced by Bragg, and are reproduced in Fig. II.7.

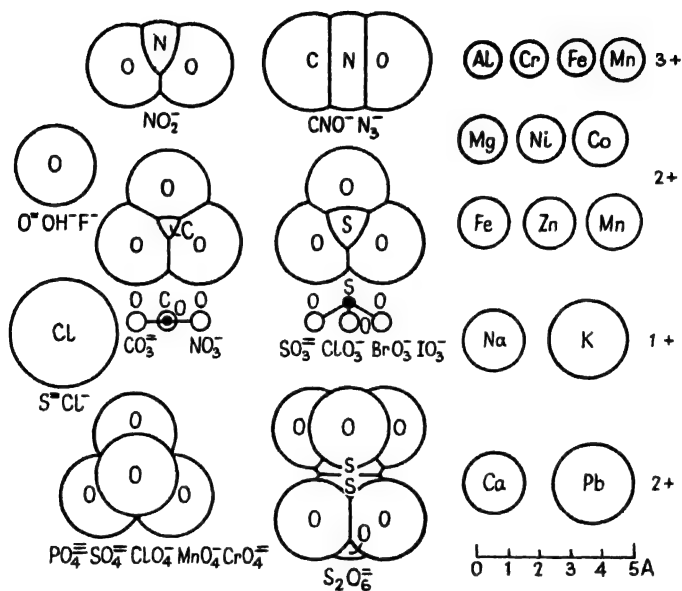


FIG. II.7. THE RELATIVE SIZES OF SOME IONS AND COMPLEX GROUPINGS (after Bragg)

(2) THE PACKING OF CO-ORDINATED UNITS IN A CRYSTAL LATTICE

All cations present in a crystal are surrounded by a certain number of anions, which are usually of larger size. From these small units of only a few ions, a crystal lattice, composed of many thousands of ions, is built up. A crystal may have cations of a single or of numerous types; so, in some cases, only one type of co-ordinated unit is present, whilst, in others, there may be several different group species. Furthermore, the linking between these units of structure must be such that the valency requirements of each ion are fully satisfied by contact with a sufficient number of ions of opposite sign.

The build-up of any crystal lattice can only be effected provided that these two principles are obeyed. There is, however, a third requirement which must be satisfied, namely, that the packing of the ions in the lattice must be tight or 'close', otherwise the crystal would not hold together.

In most silicate structures, oxygen anions predominate and are, by far, the largest ions present. These must be arranged in a crystal, so that, when they are

grouped together, they must adequately and tightly contain cations; they must also be positioned so that electrical neutrality is maintained throughout the structure; and they must also fit together so that all are firmly held by other oxygen ions in the immediate neighbourhood. The tightness of packing in a lattice is thus principally determined by the arrangement of the large spheres of oxygen atoms.

The packing of ions within a crystal lattice always tends towards a maximum, because this would give a structure of the greatest stability. The larger ions which form the essential framework are so arranged that there is the minimum of void space within the lattice as a whole. The theoretical maximum packing can result in several ways as demonstrated by Barlow, and for this treatment it is convenient to ignore the cations or smaller spheres in the assembly, and consider only large spheres of a single size and type (e.g. oxygen ions). If many uni-sized spheres are in one plane or layer, they will automatically arrange themselves as shown in Fig. II.8(a). An equilateral triangle can be drawn through the centres of any three spheres in contact and each touches six others. Each sphere touches two others in its own line and two in each adjacent line, i.e. six spheres in all. The spheres lie along sets of parallel lines which are not in one direction but in three at an angle of 60° to one another and all exactly equivalent. These lines, therefore, form a hexagonal arrangement, and this forms the closest possible packing on one plane.

To form a lattice, a series of such layers must be placed on one another so as to occupy a space of three dimensions such as a cube. Each layer may be represented by a letter A, B, C, etc.

A second layer (B) of closely-packed spheres can rest on the first layer (A) with each sphere nestling in position between three in the lower layer (Fig. II.8(b)). A third layer (C), similar in all respects to the first two, can be stacked on top of the second. At this stage two alternative arrangements can result, for the third layer can be placed in either of two positions relative to the first. Each sphere in the new layer (C) must touch three spheres in the layer (B) immediately below it, but they can go either: (i) into positions directly above the spheres in the first layer, so that the structure has each third layer identical with the first. A sequence of ABABAB, etc., fully represents the structure where A is the arrangement of spheres in one layer and B that of the layer immediately above. This is known as *hexagonal close-packing*; (ii) so that the third layer occupies entirely new positions and is unlike that of layers A and B and creates the sequence ABCABC, etc. This order would build up a pyramid and is referred to as *cubic close-packing*. Each sphere in the new layer (C) is directly above the space between three spheres in the first layer (A).

The two arrangements are in Fig. II.8 (c and d) where the arrangement of successive layers is shown.

The terms 'hexagonal' and 'cubic' close-packed refer to the shape of the resulting structures. In the former, there is a six-fold axis of rotation in a direction perpendicular to the layers so that if an imaginary axis is drawn downward through any sphere in the top layer, on rotation about this axis an identical configuration is produced six times during one complete turn of 360° . When the third layer is arranged in cubic packing there are four three-fold axes of symmetry inclined in the same way as in the body-diagonals of a cube. Rotation about an axis parallel to the body-diagonal brings the same structure into coincidence three times during a

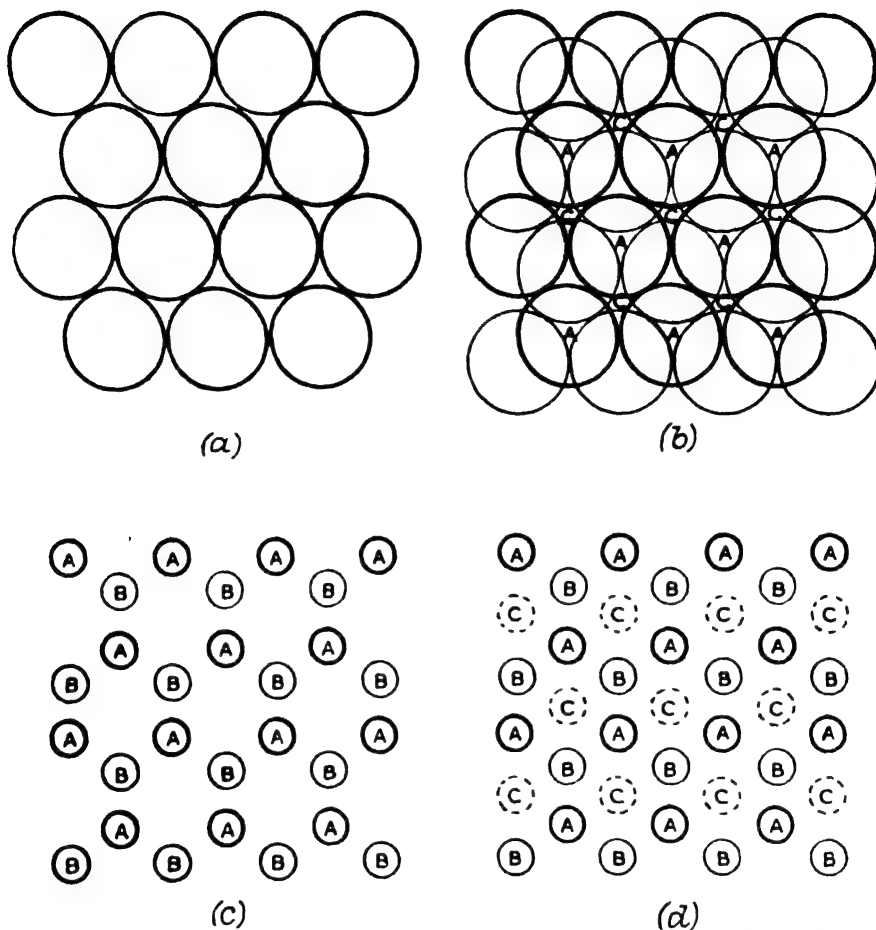


FIG. II.8. DIAGRAMMATIC REPRESENTATION OF THE CLOSE-PACKING OF SPHERES

(a) one layer of close-packed spheres; (b) two successive layers—note the available sites for the third layer marked AAA, etc., and CCC, etc.; (c) sequence of successive layers in hexagonal close-packing ABABAB, etc.; (d) successive layers in cubic close-packing ABCABC, etc.

complete turn. When the spheres are seen in plan, the layers are perpendicular to any body-diagonal of a unit cube; they are situated at the corners and mid-points of the faces of a cube, hence the alternative term *face-centred cubic* for a cubic close-packed structure.

The diagrams in Fig. II.9 illustrate these features clearly.

In both hexagonal and cubic close-packed structures, each sphere is in contact with twelve other like spheres, six of which are in the same plane and three each in the adjacent layers above and below. They differ only in the spacial arrangements of spheres in these adjacent layers.

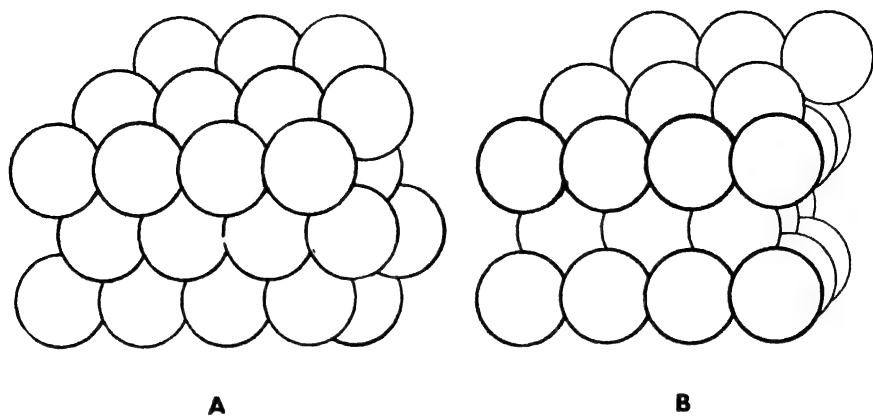


FIG. 11.9. ARRANGEMENT OF SPHERES
(A) cubic close-packing; and (B) hexagonal close-packing.

Equilateral triangles can be drawn between the centres of the spheres in the layers above and below a centrally-placed one. When the structure is hexagonal close-packed, then the apices of the two triangles point in the same direction. In cubic close-packing, the apices of the top triangle lie over the mid-points of the sides in the lower one (Fig. 11.10).

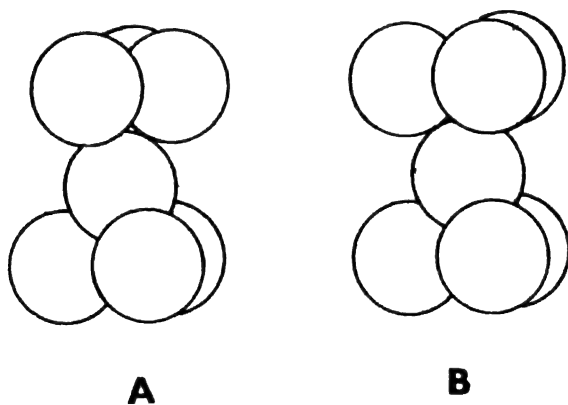


FIG. 11.10. ARRANGEMENT OF CONTACT SPHERES
(A) cubic close-packing; and (B) hexagonal close-packing.

In a third type of packing, the spheres are arranged with their centres as the corners of a cube, and another one of similar size is at the centre of the cube touching all the rest. A more open structure results, for each sphere now only touches eight others. It is called *body-centred cubic packing*, and is illustrated in Fig. 11.11.

Other arrangements are also possible; layers of close-packed spheres can be stacked in various ways, for example 'double hexagonal close-packing' ABACABAC, etc., but the environment of all atoms in the lattice cannot then be the same.

Some structures are not fully close-packed. The lattice may be so constructed that valency requirements could not be satisfied if there were not voids between the anions. Many silicate minerals have this structure.

Close-packing in crystal structures is an ideal rarely found in practice. The co-ordinated units of which the lattice is composed may be distorted by a too large or an unsymmetrical cation. Many crystals, however, have anions in approximately close-packed positions but more open than the ideal, whilst in others, the symmetrical distribution is considerably distorted.

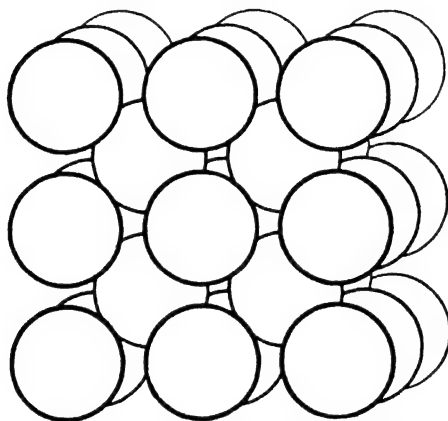


FIG. II.11. THE ARRANGEMENT OF SPHERES IN BODY-CENTRED CLOSE-PACKING

Defective Lattices. The theory of lattice structures, as described in the preceding pages, assumes that every lattice is perfect in shape and content. Many crystals show evidences of imperfect lattices and all have defects developed to a greater or less degree. In recent years, defects in the lattice have been shown to be the activation centres for solid and other reactions and will be described in detail in Chapter X.

CRYSTAL SYSTEMS

A PERFECT crystal is bounded by plane faces at constant angles to each other and the relation between such faces and angles is an important feature of the structure of all crystals. The measurement of these characteristic dimensions is one means of identifying the various compounds which occur in the crystalline form. Yet, though the angles between the faces of any crystal are constant for that substance, the shape or *habit* of those crystals may vary greatly, depending on the environmental conditions during its formation. Thus the same substance may in some occurrences be as crystals of cubic shape, but, in others, as lath- or needle-shapes and so appear to be quite different; but the various angles between the faces for all (perfect) crystals of one substance are the same irrespective of its crystalline shape.

The fundamental units of all crystals are the ions, but these are united to form larger units which give symmetry to crystals. All crystal lattices are composed of

blocks of ions arranged in a specific manner. The arrangement of ions in each block is identical and any one block in the lattice has the same spacial situation and orientation as all others.

A useful analogy which has been suggested by Bragg is that of patterned wallpaper. A particular motif repeats at regular intervals in both horizontal and vertical directions. If lines are drawn joining identical motifs then parallelograms result, all of which are regular. Each parallelogram or cell might be described as the unit of pattern, for all others are exactly the same and the wallpaper has finite extension by virtue of a number of these units being joined together.

A crystal lattice is of similar construction to the wallpaper but now there is a three-dimensional framework and the motifs may be atoms or ions or groups of them; the unit cell of pattern has now also depth, *each face* being a parallelogram. A unit cell may be outlined in several ways but it is more usual to select one which has the smallest dimensions and is in conformity with symmetry. It is defined by the length of its sides a , b and c , and by the angles between them α , β , γ . Crystallographers occasionally represent the dimensions as ratios of the crystal axes; the b axis being taken as unity.

Unit cells can be of several types depending on the lengths of the sides and the angles between them. The most unsymmetrical are those where a , b , and c are all of different lengths and α , β , γ are all different. Most crystals are composed of unit cells which are more symmetrical; the cubic type, for instance, has all sides equal and the angles between them are all right angles.

There are seven *crystal systems* in which all crystals can be classified on the basis of their symmetry and which can be related to the dimensions of the unit cell. They are:

	Axes	Angles
1. <i>Cubic</i> —which has the highest symmetry with all three axes and angles equal	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$
2. <i>Tetragonal</i> —where one axis is of unequal length but all the angles are equal, and at right angles	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
3. <i>Orthorhombic</i> —with all axes unequal but all at right angles to each other	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
4. <i>Rhombohedral</i> —with all axes equal, but the angles between them are not right angles	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$
5. <i>Hexagonal</i> —with four axes, three lateral and equal at an angle of 120° to each other, the fourth is unequal and at 90° to the plane of the lateral ones	$a_1 = a_2 = a_3 \neq c$	$\gamma_1 = \gamma_2 = \gamma_3 = 120^\circ;$ $\alpha = 90^\circ$
6. <i>Monoclinic</i> —all axes are unequal but there are two equal angles at right angles and one other not at 90°	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta$
7. <i>Triclinic</i> —this is the most unsymmetrical form with all axes and angles different	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma$

These systems refer to the external form of crystals and the unit cells may not be simple, i.e. with lattice-points situated only at corners. Additional lattice-points may be involved without altering the symmetry of the system. There are in all fourteen possibilities and these are termed the *Bravais space lattices* which are outlined in Fig. II.12. The cells numbered 1, 2, 4, 8, 9, 10, and 12 are simple; the others are either termed face- or body-centred cells. All crystals can be assigned to one or other of these space lattice groups.

This is not the complete story because the lattice-points may consist of several atoms grouped into a characteristic spacial configuration, and giving rise to different symmetry elements.

SYMMETRY ELEMENTS

A CRYSTAL which is composed of single atoms situated at the lattice-points has the greatest possible symmetry. In the simple cube (Fig. II.12), for example, the symmetry elements are as follows:

(a) Rotation about an axis drawn through the centre of two opposite faces brings the same configuration into coincidence on four occasions. There are three similar axes at right-angles to each other which permit this operation. Therefore, the cube has 3 four-fold axes of symmetry.

(b) Rotation about a body-diagonal axis results in three structure coincidences per revolution through 360° . There are four body-diagonals, hence there are 4 three-fold axes of symmetry.

(c) Rotation about an axis drawn through the centres of two opposite edges brings coincidence only twice in a complete revolution. There are six such axes. There are, therefore, 6 two-fold axes of symmetry.

(d) Planes parallel to the faces are reflection planes, for if a mirror were placed in these planes then the virtual image seen in it would be in coincidence with the actual structure behind it.

(e) Similar reflection planes occur parallel to the face-diagonals of the cube.

(f) There is a centre of symmetry or inversion because faces and edges of the cube occur in pairs on opposite sides of a central point. Any lattice-point, therefore, projected through the centre comes into coincidence with a similar point at an equal distance from the mid-point.

If the single atom or ion at the corners is replaced by a group of atoms or ions many of these symmetry elements are no longer present.

Crystals may have different groups of symmetry elements. For example, in the cubic system, spinel, rock-salt, and galena among others have all the elements outlined for the simple cube; cuprite has only a, b, and c; zinc blende and tetrahedrite have b, c, and e; pyrite has b, d, and f and in addition 3 two-fold axes; ilmenite has only b and also 3 two-fold axes, deducible from their external symmetry. Each of these groups of symmetry elements is termed a *point group* and is characteristic of a particular *crystal class*. There are five such classes possible in the cubic system and a total of thirty-two divided in the seven crystal systems.

A crystal cannot be fully defined by its point group for this refers to the symmetry of a crystal as a whole and the individual groups of atoms at a lattice-point

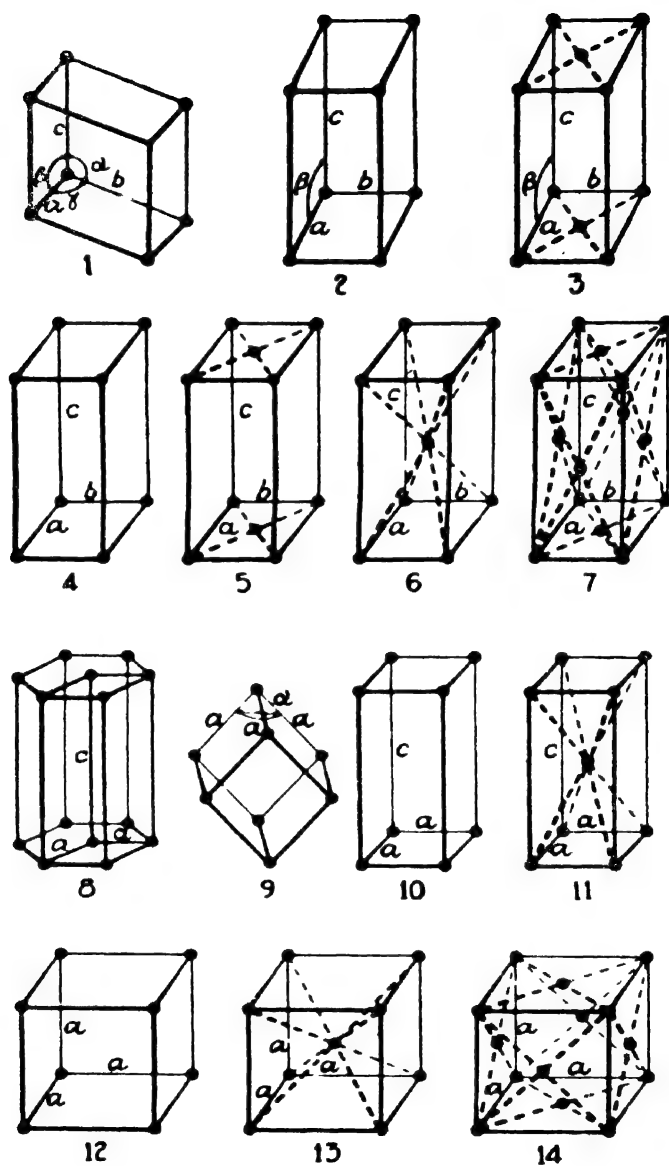


FIG. 11.12. THE FOURTEEN BRAVAIS SPACE LATTICES
 1. Triclinic; 2, 3. Monoclinic; 4, 5, 6, 7. Orthorhombic;
 8. Hexagonal, 9. Rhombohedral; 10, 11. Tetragonal;
 12, 13, 14. Cubic.
 (after Bragg)

may be quite different and yet the crystal can have the same point group. This is well demonstrated by the examples above; spinel, rock-salt, and galena have all the same point group, yet they are of entirely different chemical composition, hence the atomic grouping round each lattice-point cannot possibly be the same. The symmetry of the group itself is important and essential if a full description of the crystal is desired; it is represented by the *space group*, which shows what operations are necessary to convert a unit part of a particular arrangement or motif into the complete pattern of the unit cell. These operations involve axes of rotation, reflection planes, glide planes and screw axes, and there are a possible 230. They enable a crystal to be completely described and the positions of the symmetry operations in each of them are outlined in the International Tables for the Determination of Crystal Structure.

There have been many notations for symbolising space groups, probably the most familiar being that of Schoenflies. Hermann and Mauguin however have formulated an alternative method which describes the actual structure perhaps rather better. For a fuller space-group notation see *The Atomic Structure of Minerals* by W. L. Bragg.

THE DETERMINATION OF CRYSTAL STRUCTURES

A CRYSTAL lattice may be conceived as sets of atomic or ionic groups arranged with a certain symmetry so that planes of atoms occur throughout the lattice at equal spacings along the same crystallographic direction. Crystals behave as a three-dimensional grating which can diffract suitable radiation just as light is diffracted or 'scattered' by a 'grating' of closely-spaced objects or lines. Because these planes are of very small separation (a few Ångstrom Units at the most) radiation of comparable wavelength is required. Consequently, X-rays, which have a wavelength about ten thousand times as short as visible light, are used.

An X-ray beam, on passing through a set of lattice-points, will be diffracted and reinforcement will occur in accordance with W. L. Bragg's equation:

$$n\lambda = 2d \sin \theta$$

where n is a whole number, λ is the wavelength of the diffracted X-ray beam, d is the spacing of the planes and θ is the angle through which the beam is reflected. A series of reflections occurs from atoms in particular planes at different angles where $n = 1, 2, 3$, etc.

The characteristic X-ray pattern produced by any crystal thus enables the arrangement of the atoms in the crystal to be fully ascertained.¹

The interpretation of a pattern of a complex crystal is difficult and tedious and many minerals have not yet been completely analysed in this way.

Atomic planes can be drawn in many different ways each having its own position in the lattice and with an interplanar spacing d . It is therefore important to use a recognised nomenclature in order to produce a complete description of the structure of a crystal, including the indexing of the crystal planes.

The Miller Indices. When the system of a crystal has been determined, a diagram

¹ The theory and techniques used in X-ray analysis are described fully in Chapter V.

showing the major axes can be constructed. Thus, in a simple cubic crystal (Fig. II.13) the axes are all of equal length and are at right angles, so the a axis can be represented by the length CG, the b axis by GH and the c axis by EG. Each of these lines makes an angle of 90° with both of the others. The face ABCD cuts the a axis at C, that is, one unit from the origin G, but does not cut either the b or c dimension. The intercepts on each axis are, therefore, 1, ∞ , ∞ . These are the parameters¹ of the face ABCD and are the lengths of the intercept of this face on the a , b , c axes in turn.

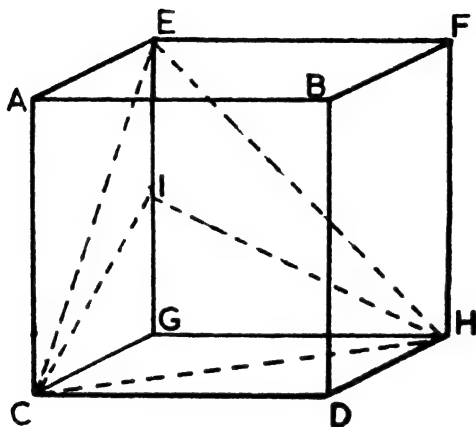


FIG. II.13. THE MILLER SYSTEM OF INDEXING CRYSTALLOGRAPHIC PLANES

In the Miller system the reciprocals of the above-mentioned parameters are used. Thus, the face ABCD has the indices $1/1$, $1/\infty$, $1/\infty$, i.e. (100). A plane CEH cuts each axis at 1, therefore it has the indices (111). The plane CIH cuts the a and b axes at 1 and the c axis at $\frac{1}{2}$; its Miller indices are therefore (112).

As a plane face must be composed of atoms or ions, the crystal lattice must be composed of planes of this type, all of which are parallel and at a characteristic distance from each other. Many sets of such planes are to be found in any one lattice, the number and type depending on the situation of the atoms, or, in other words, on the space group. The reflections recorded on an X-ray photograph of a mineral can be related to the distribution of atoms or planes of atoms, which can be represented by their Miller indices.

Crystallographic Notation and Structural Representation. It is difficult to represent a three-dimensional crystal lattice by a two-dimensional drawing. In many cases the full space-group symmetry can be visualised only by constructing a solid model. To help those readers who wish to study crystallographic features in more detail, minerals will be classified in the text, wherever possible, according to the notation adopted by Bragg, in which the space group, the crystal system and other pertinent features are tabulated. For instance, in a triclinic mineral such as the soda feldspar, *albite*, the constants can be represented as follows:

¹ A parameter is a figure representing a measurement or other datum, which is constant in the case being considered but may be different in other instances.

Albite $\text{NaAlSi}_3\text{O}_8$		System: Triclinic	
Space Group ¹ $\text{C}1$		Axes	Angles
No. of molecules per unit cell ² $Z = 4$		$a = 8.1\text{\AA}$	$\alpha = 94^\circ$
		$b = 12.9\text{\AA}$	$\beta = 116^\circ 30'$
		$c = 7.2\text{\AA}$	$\gamma = 88^\circ$

The figures on the right-hand side give the unit cell dimensions and enable the crystalline form to be constructed, and those on the left determine the relative positions of the atoms in the unit cell.

When drawing and constructing atomic models it is well to bear in mind that, although the individual atoms are extremely small, they each have a finite size and are tightly packed together. There are several methods of representing the spacial arrangement. Firstly, the model can be built up of conveniently-sized spheres, the dimensions of which are in proportion to the actual size of the atoms they portray. The result is a reproduction of the actual close-packed arrangement, but the distribution of spheres and spaces within a complex structure, where small spheres are surrounded by larger ones, may be difficult to see. The alternative is to represent atoms by points, each of which is linked to others by rods of a length in proportion to the centre to centre distance of the atoms concerned; in the resulting open network the positions of atoms in the lattice may be indicated by small spheres at the junctions of the rods. These connecting links must not be confused with the valency bonds of organic molecules for they are co-ordination linkages which indicate the spacial arrangement and the structural details of the atoms in contact. The advantage of this second method is that atomic relationships in a complex structure can be clearly seen, but the idea of the close-packing within the lattice is not shown.

There is a third method of atomic model construction which is of value in certain cases, particularly in constructing solid units. The crystal lattice is built up of a number of units which contain anions surrounding smaller cations in certain co-ordinations. These units may be equilateral triangles, tetrahedra, octahedra or cubes (depending on whether the co-ordination is three-, four-, six-, or eight-fold), so arranged as to show a pattern in which these geometrical units share corners, edges and faces with each other.

These methods are used in the following chapters; where possible the most convenient and suitable representation is shown.

¹ The space group conventional representation after Mauguin.

² All the atoms in the chemical formula (i.e. the molecular composition) must appear in the unit cell one or more times. In albite the unit cell contains 4 atoms of sodium and aluminium, 12 silicon atoms and 32 oxygen atoms.

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CHAPTER III

CRYSTAL STRUCTURE OF THE SILICATES

DESPITE the fact that the majority of minerals in the earth's crust are silicates, little was known about their fundamental structure and interrelationship until the present century was well advanced.

Until the work of Bragg (which was first published in the early 1930's), silicates were regarded as salts of hypothetical silicic acids, and as the present-day nomenclature still retains some of this earlier terminology, it is necessary to understand this system of classification in which silicates were arranged according to the ratio between the oxygen combined with the base and that combined in the acid radicles of the silicate as shown in Table III.I.

TABLE III—I. NOMENCLATURE OF THE SILICATES

Ratio of Acid Oxygen to Basic Oxygen	Formula		Metallurgical Name	Mineralogical Name
	RO Base	R ₂ O ₃ Base		
Less than 1	3RO . SiO ₂	R ₂ O ₃ . SiO ₂	{ Sub-silicate Basic silicate Singular silicate }	—
1	2RO . SiO ₂	2R ₂ O ₃ . 3SiO ₂	{ Monosilicate Sesquisilicate }	Orthosilicate
1.5	4RO . 3SiO ₂	4R ₂ O ₃ . 9SiO ₂	Bisilicate	—
2	RO . SiO ₂	R ₂ O ₃ . 3SiO ₂	Trisilicate	Metasilicate
3	2RO . 3SiO ₂	2R ₂ O ₃ . 9SiO ₂	Quadrilsilicate	—
4	RO . 2SiO ₂	—		Dimetasilicate

Orthosilicates have a ratio of acid oxygen : basic oxygen of less than 1.5-1.7. Metasilicates have a ratio greater than 1.7. In the absence of alumina the dividing line between ortho- and metasilicates is always 1.7, but where alumina is present a range of intermediate ratios occurs, due to the alumina being able to act both as an acid and as a base.

The principal theoretical silicic acids from which silicates were thought to be formed were, according to Clarke:¹

			oxygen ratio
Dimetasilicic acid	H ₂ Si ₂ O ₅	or H ₂ O . 2SiO ₂	4:1
Trisilicic acid	H ₄ Si ₃ O ₈	or 2H ₂ O . 3SiO ₂	3:1
Metasilicic acid	H ₂ SiO ₃	or H ₂ O . SiO ₂	2:1
Diorthosilicic acid	H ₆ Si ₂ O ₇	or 3H ₂ O . 2SiO ₂	1.33:1
Orthosilicic acid	H ₄ SiO ₄	or 2H ₂ O . SiO ₂	1:1

Some of these acids are unknown in nature as isolated substances but there are many compounds which appear to be salts of them.

¹ Clarke, H., *Bull. U.S. Geol. Survey*, 125, 1895.

Mellor recognised that there were numerous silicates and suggested that the corresponding acids could be arranged as in Table III.IA.

TABLE III—IIA. NOMENCLATURE OF SILICIC ACIDS (MELLOR)

Type	1 (mono-)	2 (di-)	3 (tri-)	4 (tetra-)	5 (penta-)
Ortho- Meta- (proto-) Meso- (deutero-) Para- (tritero-) Tetero- Pentero-	$H_{2n+2}Si_nO_{3n+1}$ H_4SiO_4 H_2SiO_3 — — — — — —	H_4SiO_7 ($H_4Si_2O_6$) $H_2Si_2O_5$ — — — — — —	$H_6Si_3O_{10}$ ($H_6Si_3O_9$) $H_4Si_3O_8$ $H_2Si_3O_7$ — — — — —	$H_{10}Si_4O_{13}$ ($H_8Si_4O_{11}$) $H_6Si_4O_{11}$ $H_4Si_4O_{10}$ $H_2Si_4O_9$ — — — —	$H_{12}Si_5O_{16}$ ($H_{10}Si_5O_{13}$) $H_8Si_5O_{14}$ $H_6Si_5O_{13}$ $H_4Si_5O_{12}$ $H_2Si_5O_{11}$ — — — —

The following examples show the molecular composition of various natural silicates and their classification on the basis of hypothetical silicic acids:

TABLE III—IIb. MOLECULAR COMPOSITION OF SOME SILICATES

<i>Sub-silicates</i> (oxygen ratio, less than 1:1):			
Sillimanite	$Al_2O_3 \cdot SiO_2$		
Tricalcium silicate	$3CaO \cdot SiO_2$		
<i>Orthosilicates</i> (oxygen ratio 1:1):			
Forsterite	$2MgO \cdot SiO_2$	or	Mg_2SiO_4
Fayalite	$2FeO \cdot SiO_2$		
Calcium orthosilicate	$2CaO \cdot SiO_2$		
Willemite	$2ZnO \cdot SiO_2$		
Phenacite	$2BeO \cdot SiO_2$		
Zircon	$ZrO_2 \cdot SiO_2$		
Many other orthosilicates also occur in nature.			
<i>Diorthosilicates</i> (oxygen ratio 1:33.1):			
Barysilite	$3PbO \cdot 2SiO_2$	or	$Pb_3Si_2O_7$
<i>Metasilicates</i> (oxygen ratio 2:1):			
Sodium metasilicate	$Na_2O \cdot SiO_2$	or	Na_2SiO_3
Calcium metasilicate (Wollastonite)	$CaO \cdot SiO_2$	or	$CaSiO_3$
Magnesium metasilicate (Enstatite)	$MgO \cdot SiO_2$	or	$MgSiO_3$
<i>Trisilicates</i> (oxygen ratio 3:1):			
Meerschaum	$2MgO \cdot 3SiO_2 \cdot 2H_2O$		

This theory was useful at the time as it resolved a complicated system into some semblance of order, but there were many questions still to be answered. For example, kaolinite has the formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ or $Al_2Si_2O_7 \cdot 2H_2O$. It would, therefore, be classified as a diorthosilicate derived from the theoretical acid $H_6Si_2O_7$, yet there is no resemblance in the properties of kaolinite and of other diorthosilicates. Furthermore in hydrated minerals like kaolinite the water molecules present are not in the same form as in most hydrates but are part of the actual crystal lattice. This was a little difficult to explain but some ingenious structures and linkages were postulated. The early workers in this field came very near the truth when they likened the crystal chemistry of silica to that of carbon, but they constructed their models to represent simple molecules as in organic chemistry and

assumed that the crystalline silicates were composed of groups of these molecules whereas silicate minerals are obviously crystalline and the bonds between the atoms are strong and continuous throughout the lattice.

Although modern theories have refuted the idea of silicates being the salts of complex acids, the classifications of Mellor, Asch, Tschermak and others have been shown to be correct in many details and their terminology is still widely accepted.

Modern ideas of the structure of silicates are due largely to the work of W. H. and W. L. Bragg, Pauling and Taylor. They each were responsible for ascertaining the crystal structures of many silicates, but it was W. L. Bragg¹ who first presented the complete pattern which is now generally accepted.

He postulated that all silicates are built around a unit tetrahedron, composed of a silicon ion at the centre of four symmetrically placed oxygen ions. This unit is shown in Fig. III.1 and may be chemically represented as $(\text{SiO}_4)^{4-}$. The silicon ion is quadrivalent, i.e. it has four valency shares to donate to all surrounding anions. As four oxygen ions are contained in tetrahedral grouping around each silicon ion, they each receive one valency share from the silicon. Oxygen requires two valency electrons to become completely satisfied, so each has to acquire a further unit of charge from some external source.

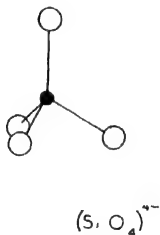
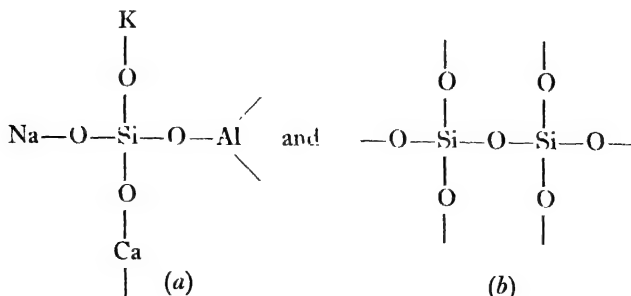


FIG. III.1. THE SILICA TETRAHEDRON

The small black circle represents a silicon ion and the large circles are oxygen ions.

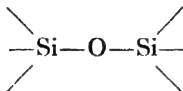
The completion of valency requirements of the oxygen can be secured by linking it to external cations of another type such as K^+ , Ca^{2+} or Al^{3+} , or to a silicon of an adjacent identical tetrahedral group, thus (figuratively):



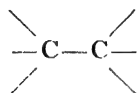
¹ Bragg, W. L., *Atomic Structure of Minerals* (Cornell Univ. Press, 1937).

The structure is by no means as simple as is represented, for the external cations in (a) are shown as being linked to only one oxygen atom¹ of a tetrahedral silica group. In actual fact they are each co-ordinated with several oxygen anions and give a fixed valency share to each. Each oxygen ion must be linked to as many cations of one or more kinds to satisfy its divalent requirements.

When an oxygen ion is linked to two silicon ions it receives one valency share from each and is thus electrically satisfied. This



linkage permits the extension of the silicate structures throughout space and is analogous to the



link of organic chemistry. The chemistry of the silicates can be likened in many respects to that of carbon for it is possible to have all the complex ring and group formations in both of them. The linkage in silicates however is through oxygen ions and not direct, and there is no double- or triple-bonding.

The type of structure of any one silicate is governed by the way in which the unbalanced oxygen valencies are satisfied. They can be divided into five groups depending on the number of oxygens of a particular tetrahedron which are linked directly to other neighbouring silica units.

STRUCTURAL FORMS OF SILICATES

(a) **Island structures** where separate $(\text{SiO}_4)^{4-}$ units exist, joined to each other only through additional cations which may be uni-, di-, tri-, or even quadrivalent. In all cases of structure formation the two rules of Pauling must apply; viz. (i) that all the cations concerned must have a certain co-ordination, governed entirely by the ratio of the size of this cation to that of the anion, and (ii) that the sum of negative charges must equal that of the positive ones; in other words, the structure must be electrically neutral. Therefore, silicates which are of the island structure type are composed of discrete tetrahedra of $(\text{SiO}_4)^{4-}$ units linked to each other only through other cations which may be in three-, four-, six-, eight- or twelve-fold co-ordination with oxygen.

There are many important minerals in this class (the orthosilicates) which are fully described later in this chapter.

(b) **Isolated group structures**, where two or more silica tetrahedra are linked together by sharing a common corner, thus introducing a Si—O—Si linkage. In this configuration, one oxygen of each tetrahedron is now completely satisfied electrically for it receives one valency share from each of the two silicon ions with

¹ The Si—O link is partly ionic, partly covalent in character, therefore it is correct to refer to the components as either atoms or ions.

which it is in contact. The remaining three oxygens attached to each silicon must receive their extra valency share from external cations as in island structures. Such a unit (represented in Fig. III.2A) has the chemical composition $(\text{Si}_2\text{O}_7)^{4-}$, so that in each unit of two tetrahedra there are six active oxygen atoms which can take part in complex formation with other cations.

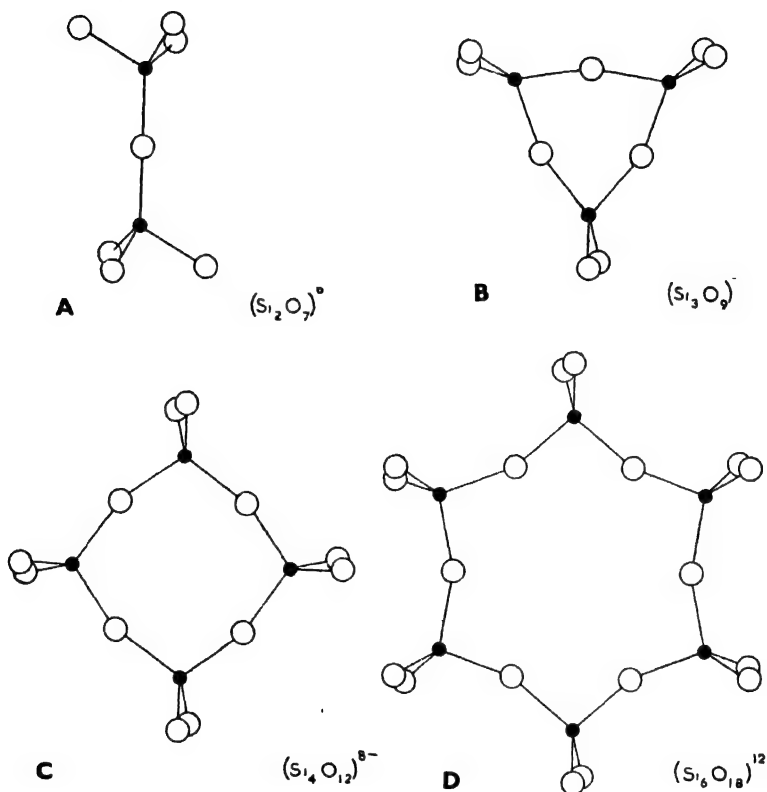


FIG. III.2. SILICA TETRAHEDRAL GROUPINGS

(a) two linked units; (b) a three-unit ring structure;
(c) a four-unit ring structure; and (d) a six-unit ring structure.

Other silicates are known which contain more complicated groupings. Thus, three tetrahedra may be linked together by sharing oxygens to form ring structures (Fig. III.2B). In this case each tetrahedron of silica $(\text{SiO}_4)^{4-}$ shares two of its oxygen atoms with similar groups, and the configuration may be expressed as $(\text{Si}_3\text{O}_9)^{6-}$, there being six oxygen ions available to combine with other cations, and the other three oxygen ions of the complex are linked to (and are electrically satisfied by) silicon atoms alone. Figs. III.2C and D show more groupings, the first being a ring of four linked tetrahedra and the second having six $(\text{SiO}_4)^{4-}$ units in the complex ring. The chemical representations are respectively $(\text{Si}_4\text{O}_{12})^{8-}$ and $(\text{Si}_6\text{O}_{18})^{12-}$.

In all cases of group structure formation the individual unit (whether composed of two, three, four or six $(\text{SiO}_4)^{4-}$ linked tetrahedra) is completely isolated from others of similar construction and is joined to another only through additional cations which are not silicon ions.

(c) **Chain structures** are formed when two oxygen atoms of every silica tetrahedron are joined to others and the resulting structure is capable of indefinite extension in the form of parallel chains (Fig. III.3(a)). Two oxygens of each tetrahedron are linked to external cations, therefore the complete chains have the general formula $n(\text{SiO}_3)^{2-}$. As each chain can be linked to other similar chains through the external cations, the structure is capable of extension in three dimensions.

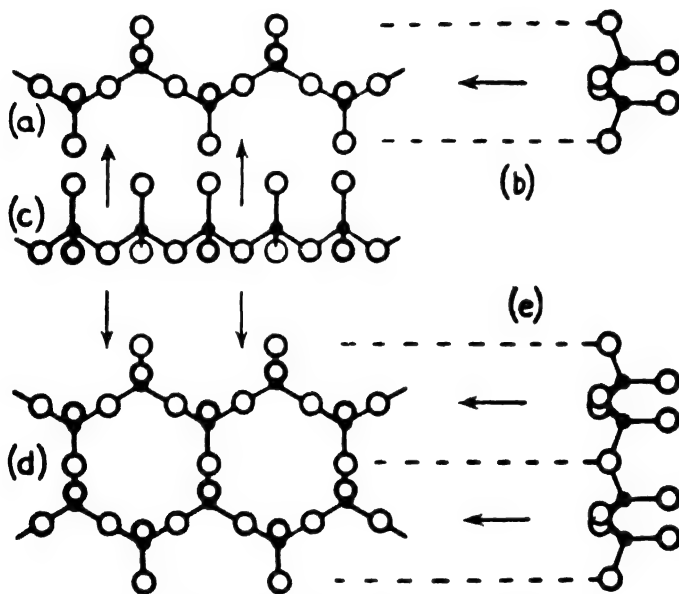


FIG. III.3. THE SILICA TETRAHEDRAL CHAIN STRUCTURES

(a), (b) and (c) the pyroxene single chain; and
(d) and (e) the amphibole double chain

Fig. III.3(d) illustrates a structure where two identical parallel chains have polymerised by sharing a further oxygen in every alternate tetrahedron. The unit is now $n(\text{Si}_4\text{O}_{11})^{6-}$ and, as shown later, it is characteristic of the *amphiboles* whereas the simple chain is exemplified by the *pyroxenes*.

(d) **Sheet structures** are the result of the linking of three oxygens of each tetrahedron with adjacent units. The structure may be visualised as the infinite extension of the amphibole double-chain formation described in the previous section. All oxygen ions are now electrically satisfied by silicon ions except one on each tetrahedron which is free to combine with external cations. As a consequence, the silica units are arranged in sheets composed of hexagonal rings and the structure

is of indefinite extension in two planes, *a* and *b*, parallel to the plane of the paper on which the base of each tetrahedron and the electrically satisfied oxygens may be supposed to rest (Fig. III.4).

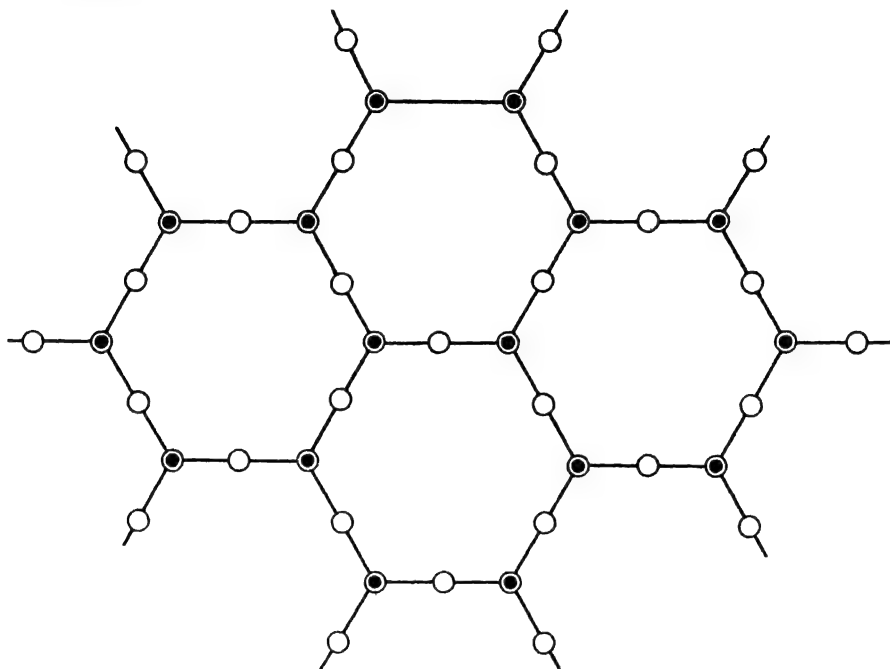


FIG. III.4. THE SILICA TETRAHEDRAL SHEET STRUCTURE

The composition of the layer can be represented by $n^2(\text{Si}_2\text{O}_5)^{2-}$; n^2 because the structure now extends in two dimensions and $(\text{Si}_2\text{O}_5)^{2-}$ is the unit expressed in its lowest terms. One hexagonal ring has six silicon atoms, although it has only a third share of each of these because they are partly contained in two other rings. Six oxygen atoms are shared between two rings, and six further oxygen atoms, which still require one valency share, are above each silicon and therefore shared between three rings. The composition of each ring is therefore

$$\frac{6\text{Si}}{3} + \frac{6\text{O}}{2} + \frac{(6\text{O}^-)}{3} \text{ i.e. } (\text{Si}_2\text{O}_5)^{2-}$$

In the ring structure of Fig. III.4 the oxygen ions which combine with other cations are shown projecting upwards in all cases. This is the assumed arrangement in most sheet-structure minerals of which kaolinite, mica and related materials are examples. The angle between $-\text{Si}-\text{O}-\text{Si}-$ must therefore be $141^\circ 34'$. There is an alternative arrangement for some clay mineral structures which implies that every alternate unsaturated oxygen points downwards and the others upwards, thereby making the $-\text{Si}-\text{O}-\text{Si}-$ angle 180° . This problem is discussed in more detail later in this chapter when the individual structures are considered.

Some sheet structures embody rings which are not hexagonal, e.g. *apophyllite* has a ring structure where only four tetrahedra are concerned.

(e) **Framework structures** represent the extreme end of the series with all four oxygen atoms of a silica tetrahedron linked directly to other silicon atoms and thus becoming part of the four-fold co-ordination of these cations. In such an arrangement, the silicon atoms entirely satisfy the valency requirements of all oxygen atoms and the structure is capable of indefinite extension in three dimensions. The ideal examples of this type of configuration are to be found in the silica minerals quartz, cristobalite and tridymite and their formulæ may be written $n(\text{SiO}_4)$ thus denoting an electrically-balanced molecule.

Silicate minerals with framework structures are not limited to the three just mentioned, for, in certain instances, aluminium atoms can replace silicon at the centre of the oxygen tetrahedra. Although this cation is of similar size to silicon and does not, therefore, cause serious distortion of the lattice, it is trivalent as against the quadrivalent cation which it has replaced. In order to restore the electrical balance of the lattice when such a replacement occurs, additional cations have to be introduced; for example, the feldspars which are composed of such a framework with aluminium replacing silicon and alkali or alkaline earth cations entering the lattice to balance the deficiency of positive charge. *Albite*, soda feldspar, is $\text{Na}(\text{AlSi}_3\text{O}_8)$ and is an example of an $\text{Na}^+\text{Al}^{3+}$ substitution for a Si^{4+} ion.

The general formula for these substituted framework structures may be written as $(\text{Si}_{(n-p)}\text{Al}_p\text{O}_{2n})^{1/2}$ where n is the total number of cations present per unit cell and p is the proportion of aluminium cations.

Titanium is also thought to substitute for silicon in framework structures, but because it is also quadrivalent the structure remains electrically balanced.

Iron also appears to replace silicon in some sheet structures.

It is possible to classify all silicates within the framework of these five groups and it is interesting to compare the predicted structures with those resulting from the hypothetical silicic acid theory. *Orthosilicates* are those which belong to the 'island' or simple group structure formation; *metasilicates* are those with simple chain linkages. More complicated silicates may have aluminium ions replacing silicon within the lattice.

1. SILICATES WITH SEPARATE SiO_4 GROUPS

IN silicate structures where each unit is connected only through extra cations, the framework is largely determined by the size of these cations and their oxygen configuration.

Small cations, like beryllium, are in four-fold co-ordination with oxygen in silicates, whilst larger cations including magnesium, ferric iron and sometimes calcium are in hexagonal or six-fold co-ordination. Still larger cations are in eight-fold grouping with oxygen, for example *zircon*, ZrSiO_4 , where the zirconium ion is surrounded by eight oxygen atoms each of which is also linked tetrahedrally to silicon. Other structures are known where the extra cations are all of one element, yet they may be co-ordinated in more than one way. Thus in the alumino-silicates of

this group, *kyanite*, *andalusite* and *sillimanite*, aluminium may be present in four-, five- or six-fold co-ordination. Complex structures also exist in which more than one cation, other than silicon, is present and each of these may have different co-ordinations.

There are two further general points: (i) the anionic configuration must be such that each oxygen receives two valency shares, one of which is provided by a silicon and the other by different cations, and (ii) the oxygen atoms (which are the largest spheres in the structure) must be as closely packed as possible.

The silicates with isolated units of $(\text{SiO}_4)^{4-}$ tetrahedra may conveniently be studied in order of increasing size of cation.

THE PHENACITE GROUP

BERYLLIUM, Be^{2+} —which is one of the smallest-sized cations with an ionic radius of 0.34 \AA —forms the silicate *phenacite*, Be_2SiO_4 . The beryllium ion is divalent and is situated at the centre of four oxygen atoms, so each co-ordinating anion receives a half valency-share from the beryllium. To achieve complete valency satisfaction, each oxygen must therefore be linked to two beryllium and one silicon atom. The complete crystal structure of phenacite is rather complicated, because the unit cell is very large, contains many cations and is of low symmetry.

The constants of phenacite¹ are:

Phenacite Be_2SiO_4	Crystal System: Rhombohedral
Space Group: $R\bar{3}$	Axis: $a = 7.68 \text{ \AA}$
$Z = 6$	Angle: $\alpha = 108^\circ 01'$

The phenacite structure typifies a number of minerals, one of which is the zinc silicate *willemitite*, Zn_2SiO_4 . In this silicate, zinc atoms replace those of beryllium in phenacite; this is rather surprising as zinc ions are much larger and should really be in six-fold and not four-fold co-ordination with oxygen. However, zinc belongs to the sub-group of elements and the outermost electron orbits can easily be distorted, and only four oxygens are spaced around the cation. The introduction of the larger cation results in an increase in the size of the unit cell. Presumably, the oxygen atoms are not as tightly compacted and an overall increase in size results. This type of expansion is of frequent occurrence and reference will be made to numerous other examples.

THE OLIVINE GROUP

WHEN the size of the extra cations in the silicate structure is increased until the size-ratio compared to oxygen is greater than 0.414 , six-fold co-ordination results. The complete structure is thus composed of silica tetrahedra linked to octahedral units. The ions of magnesium and ferrous iron are respectively 0.78 \AA and 0.83 \AA in size, and the ratio of these to oxygen is 0.58 and 0.63 respectively, so that they are well within the limits of six-fold co-ordination. As all oxygen ions which are co-ordinated to these cations receive only a third of a valency share, each must be linked to three

¹ Bragg, W. L. and Zachariasen, W. H., *Zeit. Krist.*, 72, 518, 1930.

divalent cations and also to a silicon atom if it is to receive two valency shares and thus be electrically neutralised. The *olivine group* of minerals has this configuration and many important ceramic minerals are of this class.

The mineral olivine itself is often referred to as a solid solution of magnesium and iron silicates, although the structure can be more clearly understood if olivine is imagined as magnesium silicate with some of the magnesium ions replaced by ferrous ions Fe^{2+} .

The structure of olivine is quite simple provided that the following points are remembered:

- (1) that the oxygen atoms are hexagonally close-packed,
- (2) that all silicon atoms are in tetrahedral co-ordination with oxygen,
- (3) that the cations of magnesium and iron are always in six-fold co-ordination,
- (4) that the valency of oxygen is satisfied by one share from a silicon and one-third share from each of three cations of magnesium or iron.

The ideal structure is illustrated in Fig. III.5. The oxygen atoms are hexagonally close-packed and the arrangement of the cations is clearly demonstrated; some oxygen ions have been omitted.

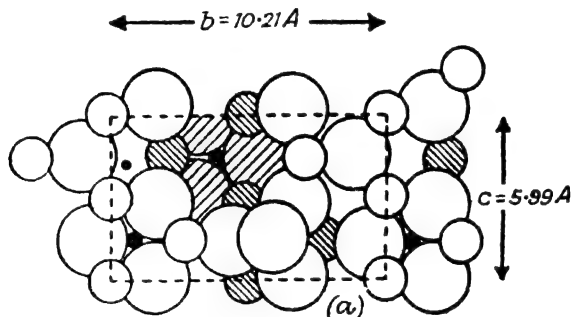


FIG. III.5. THE STRUCTURE OF FORSTERITE
(after Bragg)

The large spheres represent oxygen atoms, the small open spheres magnesium and the black spheres silicon.

Magnesium silicate (forsterite), Mg_2SiO_4 , is a commonly-occurring mineral in basic refractories and has the constants¹

Forsterite Mg_2SiO_4
Space Group: Pbnm
 $Z = 4$

System: Orthorhombic
Axes: $a = 4.77 \text{ \AA}$
 $b = 10.26 \text{ \AA}$
 $c = 5.99 \text{ \AA}$

Other similar minerals of the olivine group are shown in Table III.III. They all have the same spacial configuration and form orthorhombic crystals, but the dimensions of the unit cell are influenced by the size of cation taking part in the structure.

¹ Rinné, F., *Zeit. Krist.*, 59, 230, 1924.

TABLE III—III. LATTICE CONSTANTS OF THE OLIVINE GROUP

<i>Mineral</i>	<i>Formula</i>	<i>a</i>	<i>b</i>	<i>c</i>
Forsterite	Mg ₂ SiO ₄	4.77Å	10.26Å	5.99Å
Fayalite	Fe ₂ SiO ₄	4.80	10.59	6.16
Olivine*	(Mg.Fe) ₂ SiO ₄	4.76	10.21	5.99
Monticellite†	Mg.Ca SiO ₄	4.82	11.08	6.37

* Bragg, W. L. and Brown, G. B., *Zeit. Krist.*, 63, 538, 1926.

† Brown, G. B. and West, J., *Zeit. Krist.*, 66, 154, 1927.

The mineral *olivine* is of variable composition, as iron can replace magnesium in all proportions. The lattice constants given are for a mineral with the approximate composition (Mg_{0.9}Fe_{0.1})₂SiO₄ or 9Mg₂SiO₄.Fe₂SiO₄ expressed in more simple yet misleading terms. *Chrysolite*¹ is also an olivine; it has six times as many magnesium as iron atoms.

Monticellite, CaMgSiO₄, has a structure which is also based on olivine, but with calcium ions present in positions of six-fold co-ordination. Unlike the ferrous ions in olivine, calcium ions do not replace magnesium in all proportions. Monticellite has calcium ions only in certain positions in the lattice and the mineral is a definite compound with almost equal proportions of calcium and magnesium ions. Monticellites commonly have magnesium ions partially replaced by ferrous ions.

THE ZIRCON GROUP

THE large cation zirconium forms a silicate in which it is in eight-fold co-ordination with oxygen. Isolated (SiO₄)⁴⁻ units are present, linked only through the zirconium ion.

The contribution of the zirconium cations (Zr⁴⁺) to each surrounding anion is one-half of a valency share, so that all oxygen atoms must be in contact with one silicon and two zirconium ions in order to satisfy their valency requirements.

The structure is shown in Fig. III.6 where the unit cell is clearly tetragonal. The lattice constants² are

Zircon ZrSiO ₄	System: Tetragonal
Space Group: I4/amd	Axes: a = 6.58 Å
Z = 4	c = 5.93 Å

The eight oxygen atoms surrounding each zirconium atom are not all situated at an equal distance; four are at a distance of 2.05 Å and the others at 2.41 Å.

Thorite, ThSiO₄, has a structure similar to zircon.

¹ Whitaker, E. J. W., *Acta. Cryst.*, 5, 143, 1952.

² Wyckoff, R. W. G. and Hendricks, S. B., *Zeit. Krist.*, 66, 73, 1927.

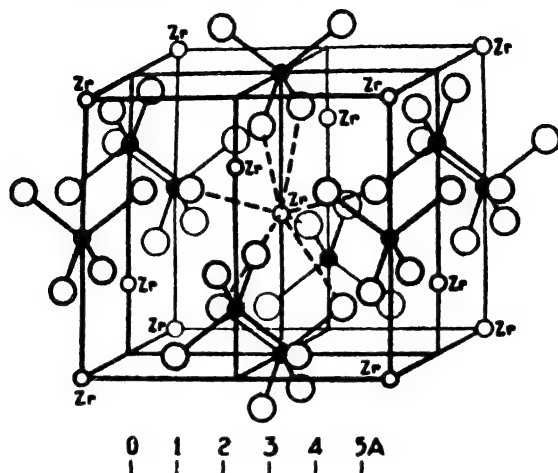


FIG. III.6. THE STRUCTURE OF ZIRCON
(after Wyckoff)

THE ALUMINO-SILICATE GROUP

IN the island structures previously described, the cations other than silicon have all been of one type or valency, and in any one group have always had the same co-ordination with oxygen, but when aluminium is the extra cation involved in silicate structures of this type, it may be in either six- or four-fold co-ordination, and in one case five-fold, which is most unusual.

There are three minerals which have the chemical composition $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$. These are *kyanite*, *andalusite* and *sillimanite*¹ and to these may be added *mullite*, $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, which has a very similar structure to sillimanite, and is a decomposition product of many alumino-silicates, and commonly occurs in fired alumino-silicate bodies.

The structure of these minerals consists of isolated units of $(\text{SiO}_4)^{4-}$ linked together by aluminium cations which, in kyanite, are all in six-fold co-ordination; in andalusite they are in both six- and five-fold and in sillimanite they are in six- and four-fold linkages.

The *kyanite* structure has only two sets of co-ordinated groupings, tetrahedrally-linked oxygen atoms round each silicon and hexagonally-positioned oxygen atoms about the aluminium ions. Furthermore, the oxygen atoms are (ideally) in a close-packed arrangement as illustrated in Fig. III.7.

A feature of the structure is the parallel chains of aluminium-oxygen linkages joined by silica units. The valency satisfaction of oxygen atoms is not simple on the basis of the proposed structure by Naray-Szabo, Taylor and Jackson; although some are linked to aluminium and silicon atoms, others are satisfied by aluminium ions

¹ Mullite so closely resembles sillimanite in properties that it was, at one time, mistaken for it and many references to 'sillimanite' in firebricks and other forms of heated clay really relate to mullite and so do many references to 'artificial sillimanite'.

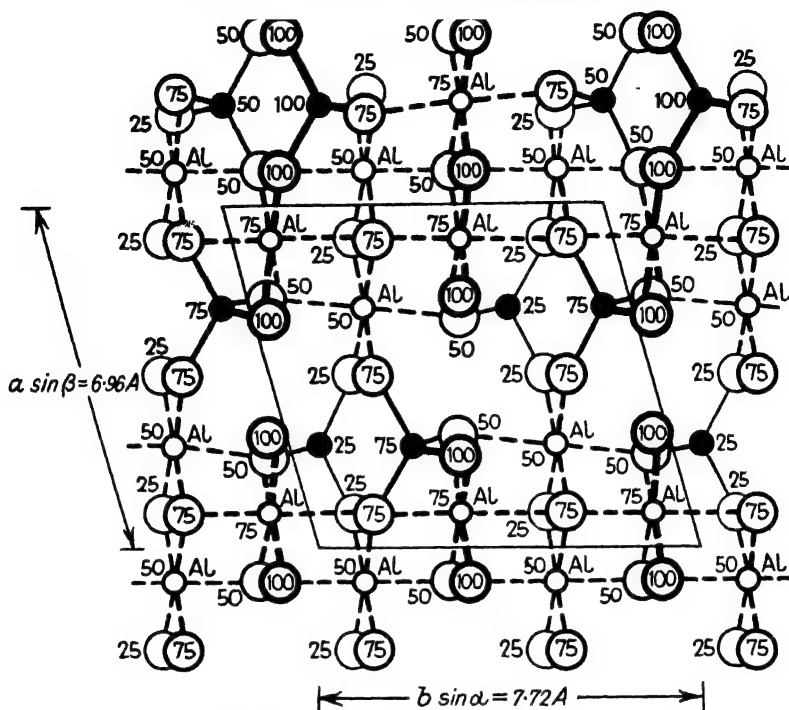


FIG. III.7. THE STRUCTURE OF KYANITE
(after Bragg)

The numbers in the circles refer to the heights of the atoms above a zero plane.

alone. Some oxygen atoms, therefore, do not belong to $(\text{SiO}_4)^{4-}$ units and the composition is best represented by the formula $\text{Al}_2\text{O}_3\cdot\text{SiO}_4$.

The structural constants¹ are

Kyanite $\text{Al}_2\text{O}_3\cdot\text{SiO}_4$
Spacc Group: Pl
 $Z = 4$

System: Triclinic

Axes:

Angles:

$a = 7.09 \text{ \AA}$ $\alpha = 90^\circ 05\frac{1}{2}'$
 $b = 7.72 \text{ \AA}$ $\beta = 101^\circ 02'$
 $c = 5.56 \text{ \AA}$ $\gamma = 105^\circ 44\frac{1}{2}'$

The structures of *andalusite* and *sillimanite* are somewhat similar to each other and are shown in Figs. III.8 and III.9; the unit cell, in both cases, is orthorhombic. Aluminium atoms are at the corners and centre of the unit cell in the projection along the c -axis. These aluminium atoms are linked to other similar atoms immediately below and above them and so there is a series of chains of aluminium-oxygen linkages running parallel to the c -axis and linked laterally by silica tetrahedra and, in andalusite, by five-fold co-ordinated aluminium and, in sillimanite, by four-fold or tetrahedrally co-ordinated aluminium.

¹ Naray-Szabo, St., Taylor, W. H., and Jackson, W. W., *Zeit. Krist.*, 71, 117, 1929.

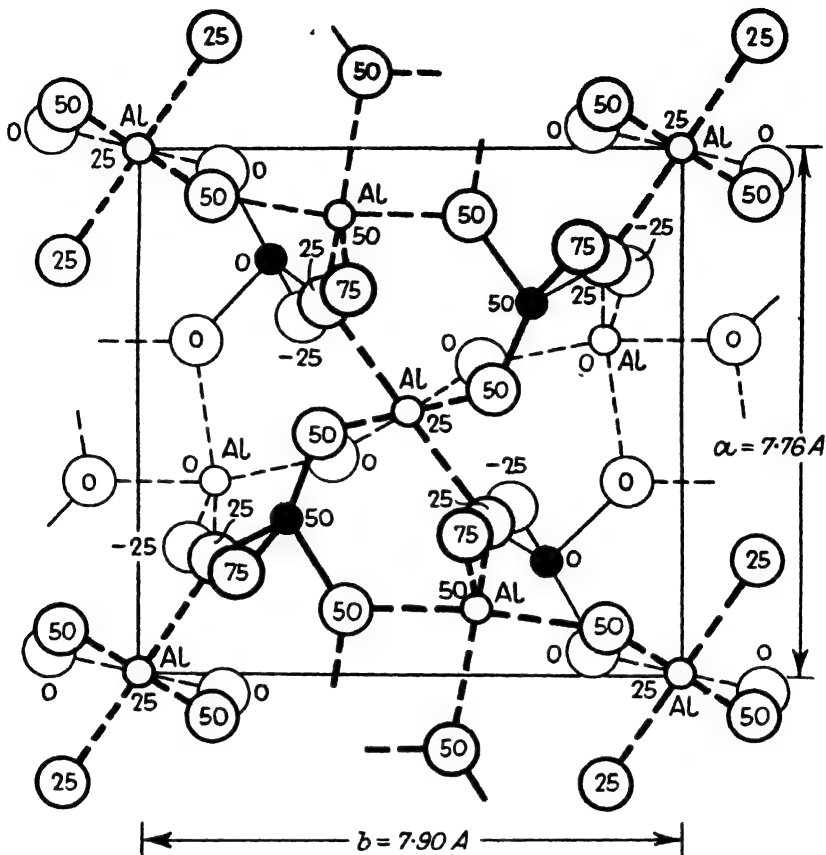


FIG. III.8. THE STRUCTURE OF ANDALUSITE
(after Hey and Taylor)

The packing of the oxygens in andalusite and sillimanite is less close than that in kyanite. The structure of sillimanite is, in fact, slightly more open than that of andalusite.

The structural constants of andalusite¹ are:

Andalusite $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$
Space Group: Pnnm
 $Z = 4$

System: Orthorhombic
Axes:
 $a = 7.76 \text{ \AA}$
 $b = 7.90 \text{ \AA}$
 $c = 5.56 \text{ \AA}$

¹ Hey, J. S. and Taylor, W. H., *Zeit. Krist.*, 80, 428, 1931.

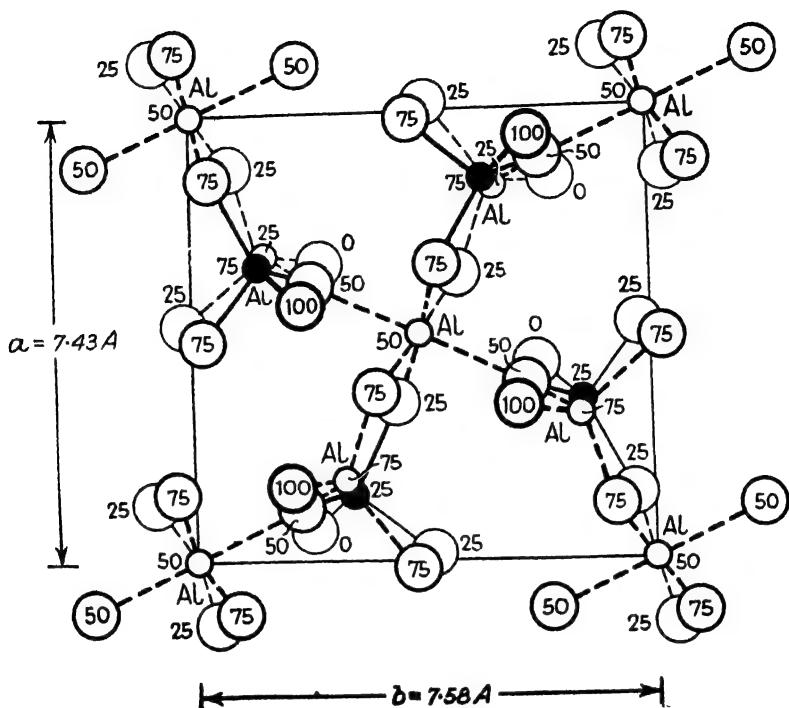


FIG. III.9. THE STRUCTURE OF SILLIMANITE
(after Taylor)

and those of sillimanite¹ are:

Sillimanite $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$
Space Group: Pbnm
 $Z = 4$

System: Orthorhombic

Axes:

$a = 7.43 \text{ \AA}$

$b = 7.58 \text{ \AA}$

$c = 5.74 \text{ \AA}$

The structure of *mullite* has not been fully worked out at present, but it is known to be closely related to sillimanite for the X-ray photographs of the two are almost identical. This is surprising because the chemical formula of mullite is quite different. As a further complication, natural and synthetic mullites have the compositions $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ and $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ respectively, yet they both give similar patterns.

The most likely explanation is that aluminium atoms can replace those of silicon in the lattice of sillimanite and Wyckoff, Greig and Bowen² have deduced from density considerations that the unit cell of mullite has the formula $\text{Al}_9\text{Si}_3\text{O}_{19\frac{1}{2}}$ as against $\text{Al}_8\text{Si}_4\text{O}_{20}$ for sillimanite. It is easy to visualise the replacement of one silicon atom by an aluminium, but the removal of one oxygen in forty is not so easy to understand.

¹ Taylor, W. H., *Zeit. Krist.*, **68**, 503, 1928, and *ibid.*, **71**, 205, 1929.

² Wyckoff, R. W. G., Greig, J. W., Bowen, N. L., *Amer. J. Sci.*, **11**, 459, 1926.

Eitel¹ has suggested that mullite may be merely a mixture of finely-divided corundum or α -alumina, Al_2O_3 , in fibrous sillimanite.

Rooksby and Partridge² have suggested that mullite may occur in at least three modifications, which differ in composition and are liable to form solid solutions.

The fact that mullite has a structure similar to sillimanite has an important bearing on the firing properties of the alumino-silicates, kyanite, andalusite and sillimanite, for all three may be converted to mullite by high-temperature calcination.

The density of these minerals is directly proportional to the closeness of packing of the oxygens, for the chemical compositions are the same. Therefore kyanite might be expected to have a greater density or specific gravity than andalusite or sillimanite, and the latter should be similar to mullite.

The densities of the minerals are:

	Kyanite	Andalusite	Sillimanite	Mullite
Density	3.59 ± 0.06	3.18 ± 0.02	3.08 ± 0.09	3.03

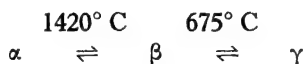
On calcination at suitable temperatures all are converted to mullite which, as shown by the different densities, involves a large volume change in kyanite but much less in the other two. So when kyanite is used as a refractory it has to be pre-calcined prior to shaping, whilst sillimanite may be used without previous heat treatment.

THE CALCIUM ORTHO-SILICATE GROUP

CALCIUM ortho-silicates are commonly-occurring minerals in refractory materials and slags, yet the relationships between them have only recently been explained. A study of their crystal structures has explained many of the perplexing changes which take place when they are heated.

There are two chemical varieties of the ortho-silicate of calcium, tricalcium silicate, $3\text{CaO} \cdot \text{SiO}_2$, and dicalcium silicate, $2\text{CaO} \cdot \text{SiO}_2$. The latter is capable of existing in at least three modifications named α , β and γ varieties.

If lime and silica are mixed in the molecular proportions of 2:1 and heated to a sufficiently high temperature both α - and β -dicalcium silicate, which have similar properties, are formed. On cooling, however, these forms convert slowly to the γ -variety with a large increase in volume. The temperature stability ranges of the different forms are given as³



Tricalcium silicate which is formed by heating lime and silica in the correct, molecular proportions is stable under normal conditions, but can be converted to β -dicalcium silicate and lime by slowly cooling between 1250°C . and 600°C . which at lower temperatures, in turn, changes into γ -dicalcium silicate.

The relationship between γ - and β -dicalcium silicate depends upon the co-ordination of calcium with oxygen at low and high temperatures. Under normal

¹ Eitel, W., *Zeit. Krist.*, **64**, 535, 1927.

² Rooksby, H. P. and Partridge, J. H., *J. Soc. Glass Tech.* (Trans.), **23**, 338, 1939.

³ Day, A. L. and Shepherd, E. S., *J. Amer. Chem. Soc.*, **28**, 1104, 1906.

conditions, calcium forms a silicate which has a similar structure to olivine, so calcium is in octahedral linkage with oxygen and the formula may be written as Ca_2SiO_4 ; its lattice constants are¹

γ -Dicalcium Silicate Ca_2SiO_4
Space Group: Pbnm
 $Z = 4$

System: Orthorhombic
Axes:
 $a = 5.06 \text{ \AA}$
 $b = 11.28 \text{ \AA}$
 $c = 6.78 \text{ \AA}$

At high temperatures, however, calcium has a different co-ordination; O'Daniel and Tscheischwili² consider that it is surrounded by four oxygens but Bredig³ has postulated that 9 or 10 anions are associated with a calcium ion, and that the structure of high-temperature dicalcium silicate is rather similar to K_2SO_4 .

The mineral *merwinite*, $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$, is considered by Bredig to have a similar structure to β -dicalcium silicate and may not be a definite compound but 'a high-temperature isomorphous mixture of forsterite in the high-temperature form of Ca_2SiO_4 '; the forsterite component may act as a stabiliser. Goldschmidt and Rait⁴ have suggested that merwinite is based on the perovskite structure (p. 196) where each calcium is surrounded by twelve oxygen atoms.

Tricalcium silicate also exists in the α , β and γ modifications but all three are similar in property and structure. The crystal structures of this mineral have not been established with certainty. O'Daniel and Hellner⁵ have suggested that the structure is based on rings of $(\text{Si}_3\text{O}_9)^{6-}$ units, but more recent work by Jeffery⁶ indicates that the mineral is similar to *alite*, $54\text{CaO} \cdot 16\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{MgO}$, which is a common constituent of cement clinker. Isolated tetrahedra of silica exist in the structure and explain the easy conversion to β -dicalcium silicate.

Jeffery has given the lattice constants of tricalcium silicate as

Tricalcium Silicate $3\text{CaO} \cdot \text{SiO}_2$
Space Group: R3m
 $Z = 9$

System: Pseudo-rhombohedral
(hexagonal)
Axes:
 $a = 7.0 \text{ \AA}$
 $c = 25.0 \text{ \AA}$ } for hexagonal cell

THE GARNET GROUP

SILICATE minerals are known where isolated $(\text{SiO}_4)^{4-}$ units are linked to more than one type of cation. The best example is the mineral group, *garnet*, which has the general formula $\text{R}_3^{2+}\text{R}_2^{3+}(\text{SiO}_4)_3$ where R^{2+} is a divalent cation such as Ca, Mg or Fe^{2+} or Mn, and R^{3+} is a trivalent cation like Al, Cr, Fe^{3+} .

The structure is rather complex as there are tetrahedrally co-ordinated groups of oxygen atoms around each silicon, octahedral units around trivalent cations and

¹ O'Daniel, H. and Tscheischwili, L., *Zeit. Krist.*, 103, 178, 1941.

² O'Daniel, H. and Tscheischwili, L., *Zeit. Krist.*, 104, 124, 1942.

³ Bredig, M. A., *Amer. Miner.*, 28, 594, 1943.

⁴ Goldschmidt, H. J. and Rait, J. R., *Nature*, 152, 356, 1943.

⁵ O'Daniel, H. and Hellner, E., *Neues J. Min. Geol. Paläont.* 5, 108, 1950.

⁶ Jeffery, J. W., *Acta Cryst.*, 5, 26, 1952.

oxygen atoms in eight-fold co-ordination round divalent ones. Every oxygen atom is linked to one silicon atom, one trivalent ion, and to two divalent cations. The valency contribution from each is thus 1, $\frac{1}{2}$ and two $\frac{1}{2}$'s respectively, making a total of 2. The unit cell is cubic and varies in size with the cations present.

The structural constants of the group are¹

Garnet $\text{R}_3^{2+}\text{R}_2^{3+}(\text{SiO}_4)_3$
 Space Group: $\text{Ia}3\text{d}$
 $Z = 8$

System: Cubic
 Axis: a —variable but about 12 \AA

An unusual feature of the garnet group is that hydroxyl units can apparently replace $(\text{SiO}_4)^{4-}$ tetrahedra. Artificial hydrogarnets² have been prepared, one of which has the composition $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$, but is structurally similar to *grossularite*, $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$.

Titanite, $\text{CaTiO}_3\text{SiO}_4$, also contains isolated $(\text{SiO}_4)^{4-}$ tetrahedra which are linked to titanium ions in octahedral co-ordination with oxygen and to calcium ions which are within groups of seven. Titanite is a commonly occurring mineral, although it is sparsely distributed. Titanite (or *sphene*) is often the source of titanium in volcanic and metamorphosed rocks. The crystals are monoclinic with the structural constants³

Titanite $\text{CaTiO}_3\text{SiO}_4$
 Space Group: $\text{C}2/c$
 $Z = 4$

System: Monoclinic
 Axes: Angle:
 $a = 6.55 \text{ \AA}$
 $b = 8.70 \text{ \AA}$ $\beta = 60^\circ 17'$
 $c = 7.43 \text{ \AA}$

The mineral *topaz* is an aluminosilicate containing fluorine and is sometimes used as a refractory material after the fluorine has been driven off by heat and mullite formed.

In topaz, isolated units of silica tetrahedra are present linked to aluminium ions which are in six-fold co-ordination, but the surrounding anions are not all the same. Four are oxygen atoms and the remaining two are fluorine atoms which are shared between two adjacent octahedra. The oxygen atoms are close-packed, but not in a simple form.

The structural constants⁴ are

Topaz $(\text{AlF})_2\text{SiO}_4$
 Space Group: Pbnm
 $Z = 4$

System: Orthorhombic
 Axes:
 $a = 4.64 \text{ \AA}$
 $b = 8.78 \text{ \AA}$
 $c = 8.37 \text{ \AA}$

Other minerals exist which have separate $(\text{SiO}_4)^{4-}$ tetrahedra but they are not of importance as ceramic materials.

¹ Menzer, G., *Zeit Krist.*, 63, 157, 1926, and 69, 300, 1928.

² Flint, E. P., McMurdie, H. F. and Wells, L. S., *J. Res. Nat. Bur. Stand.*, 26, 13, 1941.

³ Zachariasen, W., *Zeit. Krist.*, 73, 7, 1930.

⁴ Pauling, L., *Proc. Nat. Acad. Sci.*, 14, 603, 1928.

Alston, N. A. and West, J., *Zeit Krist.*, 69, 149, 1928.

2. SILICATES WITH COMPLEX SILICON-OXYGEN GROUPS

COMPLEX silicon-oxygen groups may be of many types, so the structures which are included in this group may differ widely. Although there is no important family of minerals with structures of this type, some compounds frequently associated with slags and high-fired ceramic products undoubtedly contain isolated complex groupings.

As explained in the earlier part of the chapter, the complex groups most commonly occurring are (i) those with two linked tetrahedra $(\text{Si}_2\text{O}_7)^{6-}$, (ii) those with three tetrahedra arranged in the form of a ring giving the group $(\text{Si}_3\text{O}_9)^{6-}$, (iii) those with four tetrahedra in a ring $(\text{Si}_4\text{O}_{12})^{8-}$, and (iv) those with hexagonal rings or groups of $(\text{Si}_6\text{O}_{18})^{12-}$.

STRUCTURES WITH $(\text{Si}_2\text{O}_7)^{6-}$ GROUPS

SIMPLE structures are known where one type of cation satisfies the valency requirements of the groups and provides a linking ion for a three-dimensional network. Such an example is the rare mineral *thortveitite*, or scandium silicate, $\text{Sc}_2\text{Si}_2\text{O}_7$, but in general, greater complexity in structure is more usual.

The *Melilite Group* includes minerals which are the result of slag attack at a high temperature on silicate refractories. A range of solid solutions exists with *gehlenite*, $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, as one end-member and *akermanite*, $2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$, as the other. Alkali ions and ferrous iron ions may also replace other cations and enter the complex.

The structure is based on groups of two silica tetrahedra sharing a common corner, but as aluminium ions can replace silicon ions at the centre of four oxygen atoms, the groups have the general formula $(\text{Si}, \text{Al})_2\text{O}_7$. Magnesium ions are also within a tetrahedral group of oxygen atoms and calcium is in eight-fold co-ordination. The full structural formula may be represented as $(\text{Ca}, \text{Na})_2(\text{Mg}, \text{Al})_1(\text{Si}, \text{Al})_2\text{O}_7$, so on this basis gehlenite is $\text{Ca}_2\text{Al}(\text{Si}_1\text{Al}_1)\text{O}_7$ and akermanite is $\text{Ca}_2\text{MgSi}_2\text{O}_7$. The replacement may be imagined as $\text{Al} + \text{Al}$ for $\text{Mg} + \text{Si}$. This is a common form of substitution in other silicates. The crystal form of the melilites¹ is tetragonal with a space group of $\text{P4}_2\text{1m}$.

STRUCTURES WITH ISOLATED $(\text{Si}_3\text{O}_9)^{6-}$ RINGS

THE well-known example of structures with isolated rings of $(\text{Si}_3\text{O}_9)^{6-}$ units is the mineral *benitoite*, $\text{BaTiSi}_3\text{O}_9$. Titanium and barium atoms lie within groups of six oxygen atoms.

Calcium metasilicate or *wollastonite*, CaSiO_3 , is thought to belong to this group, although from the formula it could be classified as a pyroxene with a chain formula. Barnick² however suggests that the mineral is best represented by the formula $\text{Ca}_3\text{Si}_3\text{C}_9$ indicating groups of $(\text{Si}_3\text{O}_9)^{6-}$ rings linked through calcium ions. Three

¹ Warren, B. E., *Zeit. Krist.*, 74, 131, 1930.

² Barnick, M., *Struct. Ber. (Abs.)*, 4, 207, 1936.

modifications of this mineral have been recognised, *pseudo-wollastonite* or α -CaO.SiO₂ and two forms of β -CaO.SiO₂, *wollastonite* and the less common *para-wollastonite*. The last variety has not been studied in detail but as the normal beta-variety closely resembles it in its properties, it is probable that the lattice configurations are similar.

Wollastonites are common in lime-slugs and often crystallise from lime glasses. The α -variety which is monoclinic is metastable below 1200° C., when it converts slowly to the β -varieties. In many ways, wollastonites are similar to the pyroxenes, but the unit cell has no relationship to that of diopside, CaMg(SiO₃)₂.

The lattice constants of wollastonite are

Wollastonite CaSiO ₃ (or Ca ₃ Si ₃ O ₉)	System: Triclinic
Space Group: P $\bar{1}$	Axes: Angles:
Z = 6 (or 2)	a = 7.88 Å α = 90°
	b = 7.27 Å β = 95° 16'
	c = 7.03 Å γ = 103° 25'

STRUCTURES WITH (Si₄O₁₂)⁸⁻ RINGS

THE best known examples of minerals with four silica tetrahedra arranged in the form of a ring are certain *zeolites*. Aluminium ions are present also in tetrahedral units, therefore it is better to regard zeolites as framework silica structures with aluminium ions replacing some silicon and to include them in the appropriate section of this chapter.

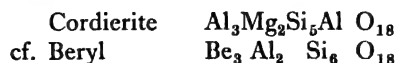
STRUCTURES WITH (Si₆O₁₈)¹²⁻ RINGS

THE important source of beryllia for refractory purposes is the mineral *beryl*, 3BeO.Al₂O₃.6SiO₂, which is composed of symmetrically-placed rings of six silica tetrahedra linked to other similar groupings through beryllium and aluminium ions. The structure is illustrated in Fig. III.10; beryllium atoms are in tetrahedral co-ordination whilst aluminium atoms are at the centre of six oxygen atoms. Each 'valency' oxygen is linked to one silicon, one aluminium and one beryllium atom.

The lattice constants¹ are

Beryl Be ₃ Al ₂ Si ₆ O ₁₈	System: Hexagonal
Space Group: C6/mcc	Axes:
Z = 2	a = 9.21 Å
	c = 9.17 Å

The mineral *cordierite*, 2MgO.2Al₂O₃.5SiO₂, which is of frequent occurrence in steatite-clay bodies, has been shown by Bystom² to be based on the beryl structure. One silicon atom in every ring of six is replaced by an aluminium atom and the chemical representation is



¹ Bragg, W. L. and West, J., *Proc. Roy. Soc.*, **A111**, 691, 1926.

² Bystom, A., *Arkiv. Kemi. Min. Geol. Stockholm*, **15B**, 12, 1942.

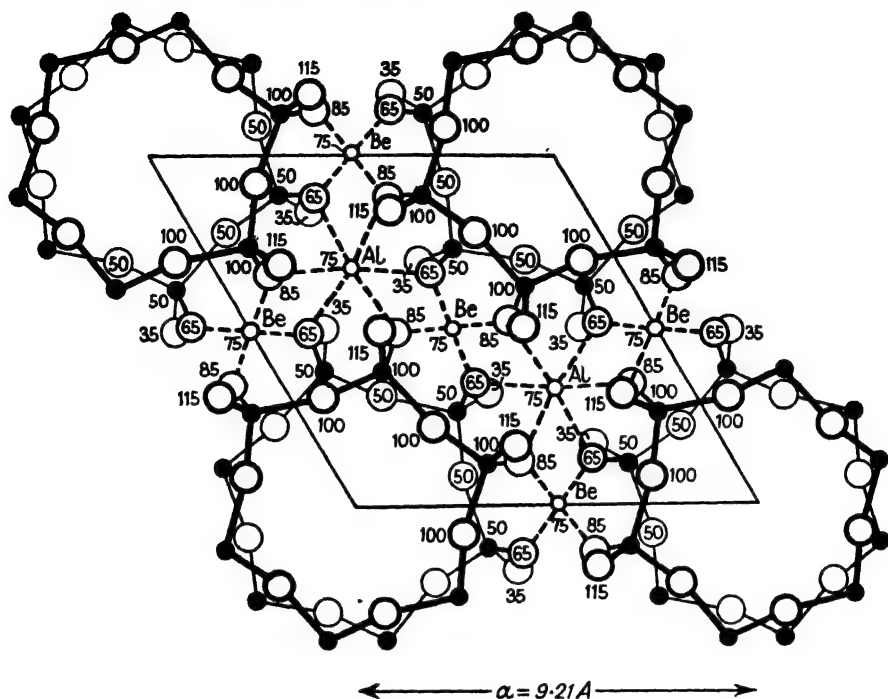


FIG. III.10. THE STRUCTURE OF BERYL
(after Bragg and West)

There are three forms α , β and μ of cordierite, all of which form fibrous crystals. The β - and μ -forms revert to the α -variety when heated to 830–1050° C. The α -form (which is the commonest) is pseudo-hexagonal. Ferrous iron can replace magnesium in the structure to form iron cordierite, which occasionally occurs in imperfectly-fired fireclay materials and in blast-furnace hearth bricks.¹

The structure of the mineral *tourmaline* is also based on isolated units of hexagonal rings of six silica tetrahedra. Tourmaline is a silicate of boron and aluminium, although replacements by other cations are frequent. The mineral is commonly associated with china clays as it is a primary mineral of granites and pegmatites.

3. SILICATES WITH CHAINS OF SILICON-OXYGEN LINKAGES

MINERALS with chain structures are limited entirely to the pyroxenes and amphiboles, with the exception of a few examples which are intermediate between true amphiboles and layer structure minerals.

Within the pyroxene and amphibole group many minerals are classified which

¹ Rigby, G. R., *The Thin-section Mineralogy of Ceramic Materials* (B.C.R.A., 1953).

TABLE III—IV. IMPORTANT MINERALS OF THE PYROXENE AND AMPHIBOLE GROUPS

<i>Pyroxenes</i>		<i>Amphiboles</i>
<i>Orthorhombic</i>		
{ Enstatite Hypersthene	MgSiO ₃ (Mg,Fe)SiO ₃	Anthophyllite (OH) ₂ (Mg,Fe) ₇ Si ₈ O ₂₂ Antholite (OH) ₂ Na ₂ Ca(Mg,Fe) ₅ Si ₈ O ₂₂
<i>Monoclinic</i>		
{ Clinoenstatite Clinohypersthene Ferrosilite Diopside Hedenbergite Augite	Mg ₂ Mg(SiO ₃) ₂ (Mg,Fe) ₂ (SiO ₃) ₂ Fe ₂ Fe(SiO ₃) ₂ CaMg(SiO ₃) ₂ CaFe ²⁺ (SiO ₃) ₂ Ca(Mg,Fe ²⁺)SiSiO ₆	Tremolite (OH) ₂ Ca ₂ Mg ₅ Si ₈ O ₂₂ Actinolite (OH) ₂ Ca ₂ (Mg,Fe ²⁺) ₅ Si ₈ O ₂₂ Ferrotremolite (OH) ₂ Ca ₂ Fe ₅ ²⁺ Si ₈ O ₂₂ Soda-Tremolite (OH) ₂ CaNa ₂ Mg ₅ Si ₈ O ₂₂ Hornblende (OH) ₂ Ca ₂ Na(Mg,Fe,Al) ₆ Al ₃ Si ₆ O ₂₂ { (OH) ₂ Ca ₂ (Mg,Fe,Al) ₅ AlSi ₇ O ₂₂ Küpferrite (OH) ₂ Mg ₇ Si ₈ O ₂₂ Grunerite (OH) ₂ Fe ₇ Si ₈ O ₂₂ Glaucophane (OH) ₂ Na ₂ (Mg,Fe ²⁺) ₃ (Al,Fe ³⁺) ₂ Si ₈ O ₂₂ Riebeckite (OH) ₂ Na ₄ Fe ₃ ²⁺ +Fe ₃ ³⁺ +Si ₈ O ₂₂
Acmite Jadeite Spodumene	Mg(Al,Fe ³⁺)AlSiO ₆ NaFe ³⁺ (SiO ₃) ₂ NaAl(SiO ₃) ₂ LiAl(SiO ₃) ₂	

vary widely in composition. Their relationships can be established by their optical properties and the type of X-ray pattern.

The *pyroxene group* of minerals may be represented by the general formula $R^{2+}SiO_3$,¹ but the degree and type of substitution is complex. The R^{2+} cation, for example, can be replaced by Al^{3+} and Fe^{3+} and aluminium ions can take the place of silicon in any ratio up to about 1 in 3. Pyroxenes crystallise in several classes, some of which have not been fully analysed. Pyroxenes are present in slags and refractory materials, and they can invariably be identified in magnesites or chrome-magnesites which have been exposed to a siliceous iron-bearing slag at a high temperature.

Amphiboles are similar in composition and it is impossible to differentiate them from pyroxenes by chemical analysis alone. This is to be expected as amphiboles are based on a unit of $(Si_4O_{11})^{6-}$ and pyroxenes on a unit of $(SiO_3)^{2-}$; aluminium may replace silicon, thus adding further confusion. Some guide to the type of mineral is given by the loss of water on calcination, because hydroxyl groups are essential constituents of the structure of amphiboles, although fluorine atoms sometimes replace them. The main difference between the groups is the angle between the cleavage planes of the crystals which in pyroxenes is 93° and in amphiboles, 56° . This point is dealt with in more detail in Chapter V.

¹ The group is known as the metasilicates, a term which dates back to the days when silicates were classified as salts of hypothetical silicic acids (p. 98).

Crystallographically, pyroxenes are made up of single chains of linked silica tetrahedra. Each of the units in the chain has two oxygens out of four shared with other similar tetrahedra; the other two oxygen atoms are connected to other cations and receive a full valency share to be electrically neutral. The chains may be of indefinite length and are linked to others through the extra cations. The bond angle between the Si—O—Si linkage is about 141° , hence the 'unsatisfied' oxygen atoms of each tetrahedron lie in the same planes.

In the amphibole structure two parallel pyroxene chains are directly joined through an oxygen of every alternate tetrahedron. Once again the double chain is continuous from left to right, but is limited in the directions at right-angles where linkage must be through other cations.

A comparison of the two units is given in Fig. III.3(a) and (b). The upper diagram is the pyroxene chain viewed in plan, in elevation and end on; the lower shows the amphibole unit from the same aspects.

The crystals of both pyroxenes and amphiboles are lath- or needle-shaped, and in some cases fibrous. This is a direct result of the preferential development along the chain length.

The two groups can be conveniently divided into sub-sections on the basis of their crystal form. Both pyroxenes and amphiboles crystallise mainly in either the orthorhombic or monoclinic classes, and Table III. IV summarises some of the main types.

The table includes only a few known pyroxenes and amphiboles, but it does indicate their comparative complexity of composition. Most of the end members form solid solutions with others; the main series are indicated by brackets.

THE PYROXENES

THE solid solution series enstatite-hypersthene is probably the most common group of naturally occurring pyroxenes. The minerals are orthorhombic at normal temperatures, but at high temperatures transform to the monoclinic clino-varieties. The structure of orthorhombic *enstatite* is shown in Fig. III.11, *hypersthene* and *ferrosilite* are similar but with some iron replacing magnesium ions. The three-dimensional nature of the crystal is illustrated, because the magnesium ions, which are in six-fold co-ordination with oxygen, link four chains, the top two of which have silicon atoms at positions 65 and 85 above a zero plane. The lower two chains have silicon atoms at 15 and 35. The uppermost chain has its vertices lying in opposite directions to those in the lower one.

The structural constants of a *hypersthene* which contains 30 per cent FeSiO_3 and 70 per cent MgSiO_3 , are, according to Warren and Modell:¹

Hypersthene (Mg, Fe) SiO_3 ,
Space Group: Pbca
 $Z = 16$

System: Orthorhombic
Axes:
 $a = 18.20 \text{ \AA}$
 $b = 8.86 \text{ \AA}$
 $c = 5.20 \text{ \AA}$

¹ Warren, B. E. and Modell, D. I., *Zeit. Krist.*, 75, 1, 1930.

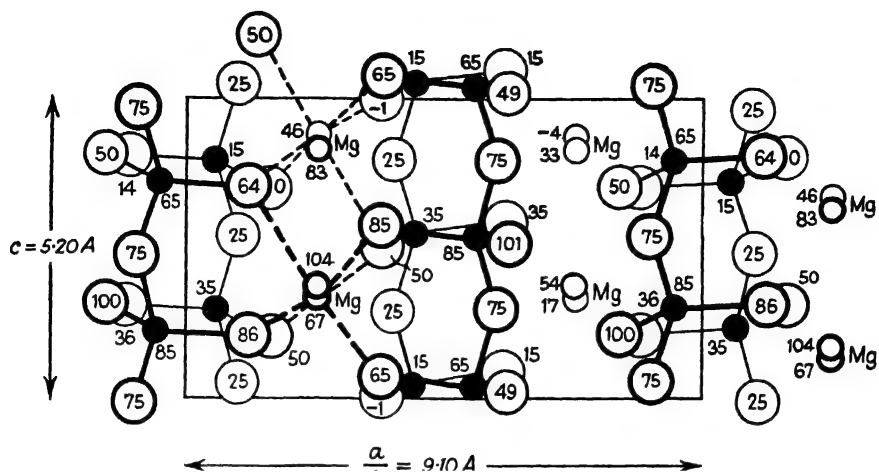


FIG. III.11. THE STRUCTURE OF ENSTATITE
(after Bragg)

The pyroxene chain runs parallel to the c -direction. The figures in the circles denote the height of atoms above a zero plane.

Diopside in solid solution with clinoenstatite is of common occurrence in dolomites, particularly when they have been in contact with silica slags. Ferrous iron may also be present in solid solution.

The crystal structure of diopside is similar to enstatite, except that the chains are not so symmetrically positioned, and the structure becomes monoclinic. Calcium and magnesium ions link adjacent chains, but the former is within a group of eight oxygens as against six around magnesium. Calcium is in contact with six 'active' oxygens and two 'inactive' anions which are links in silicon-oxygen chains.

The structural constants have been given by Bragg and Warren¹ as

Diopside $\text{CaMg}(\text{SiO}_3)_2$
Space Group: $C2/c$
 $Z = 4$

System: Monoclinic
Axes: Angle
 $a = 9.71 \text{ \AA}$
 $b = 8.89 \text{ \AA}$ $\beta = 74^\circ 10'$
 $c = 5.24 \text{ \AA}$

The other pyroxenes *augite*, *acmite* and *jadeite* are of similar structure to diopside, but the lithium pyroxene *spodumene* has apparently a slight distortion due to the small size of the alkali ion.

In pyroxenes, typical isomorphous replacements are Fe^{2+} for Mg^{2+} , Al^{3+} (oct.) for Mg^{2+} and Al^{3+} (tetr.) for Si^{4+} , with some Fe^{3+} replacing Al^{3+} (oct.).

THE AMPHIBOLES

THIS group is important because some of the amphibole minerals are fibrous in habit and are a common form of *asbestos*. The three main asbestos minerals of the

¹ Warren, B. E. and Bragg, W. L., *Zeit. Krist.*, 69, 168, 1928.

amphibole group are *anthophyllite*, *tremolite*, and *riebeckite*. The crystal structures are similar, with anthophyllite bearing the same relation to enstatite as tremolite to diopside.

The structural constants of tremolite¹ are

Tremolite $(\text{OH})_2\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}$	System: Monoclinic
Space Group: $C2/m$	Axes: Angle:
$Z = 2$	$a = 9.78 \text{ \AA}$
	$b = 17.8 \text{ \AA}$ $\beta = 73^\circ 58'$
	$c = 5.26 \text{ \AA}$

If the unit cell dimensions are compared with those of diopside it is obvious that the only material difference is a doubling along the *b*-crystallographic axis.

In the tremolite structure Fig. III.12 there are large voids unoccupied by any cations; this enables one of the two Ca^{2+} ions to be replaced by two Na^+ ions, one-half of the Na^+ replacing the Ca^{2+} and the other half of the Na^+ ions entering the voids.

This is an ideal picture of the structure of an amphibole; the position of the cations and hydroxyl units with respect to the silica chain is also of great importance. In order that the cations may have the correct co-ordination and that the structure shall be electrically balanced, hydroxyl (OH) groups must be linked to the magnesium ions and receive a third of a valency share from three of them.

Isomorphous replacement occurs as in pyroxenes, so that in a typical amphibole, such as hornblende, there are the pyroxene replacements and also $\text{Na}^+ + \text{Al}^{3+}$ (oct.) for $\text{Ca}^{2+} + \text{Mg}^{2+}$, $\text{Ca}^{2+} + \text{Al}^{3+}$ (tetr.) for $\text{Na}^+ + \text{Si}^{4+}$ and F^- for $(\text{OH})^-$.

In the amphibole hornblende, aluminium ions replace silicon in the chains, thereby creating a valency deficiency. Although this is counterbalanced to some extent by further aluminium substituting for magnesium ions, balancing ions, such as Na and K, enter the lattice and are situated at the points marked AA'.

Chrysotile, the serpentine mineral, was thought until quite recently to be an amphibole, but it is now known to have a layer-silicate lattice (see p. 139).

There is one group of clay minerals which has a similar structure to the amphiboles. This is the mineral group which was originally termed *palygorskite* by Russian workers. More recently, minerals of this same group, of American origin, have been named *attapulgites*.

Palygorskites, which are usually fibrous in texture, are complex hydrated magnesium silicates often with considerable amounts of aluminium, calcium and iron. Bradley² has described the structure as amphibole-like which is more feasible than the mica-like structure originally suggested.

Fig. III.13 is a diagrammatic representation of the structure of palygorskite viewed along the *c*-axis. The amphibole double chains run along the *c*-direction, that is, downwards through the plane of the book, therefore the chains are shown in the end-on position. Palygorskite differs from a true amphibole in that each double chain is linked directly to similar ones in the lateral direction, but each alternate chain has its vertices (valency electrons) pointing in opposite directions. Thus, there

¹ Warren, B. E., *Zeit. Krist.*, 72, 42, 1929.

² Bradley, W. F., *Amer. Min.*, 25, 405, 1940.

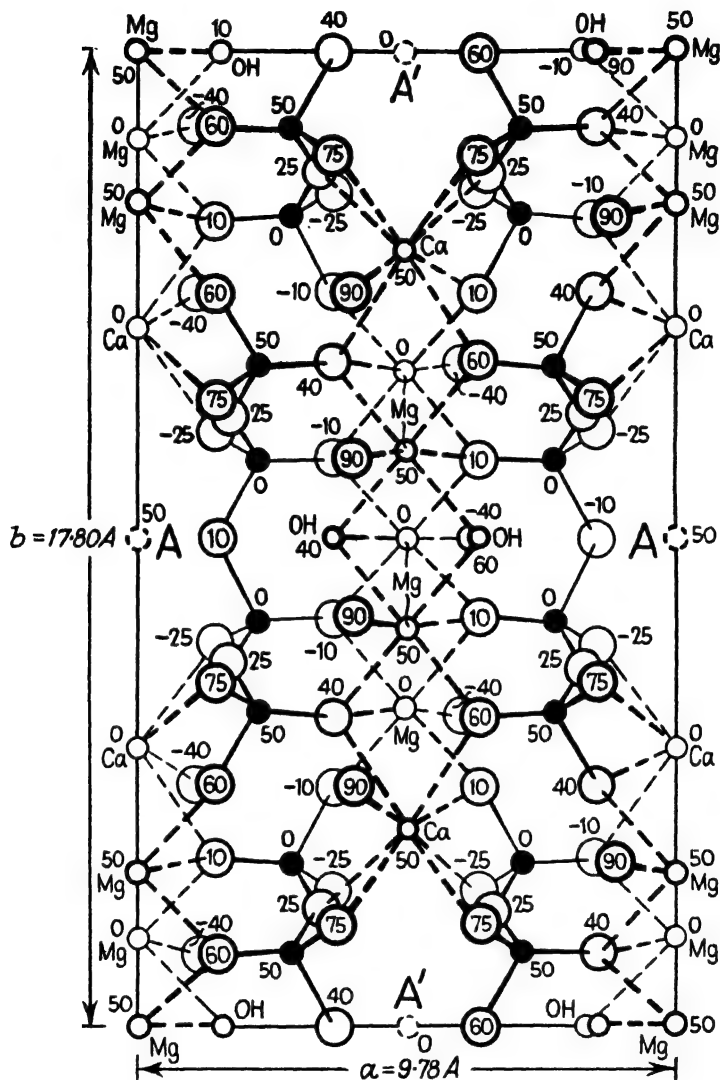


FIG. III.12. THE STRUCTURE OF TREMOLITE

The amphibole double chains run parallel to the b -dimension. The small numbers refer to the height of atoms above a zero plane.

are continuous sheets of silicon-oxygen linkages, but they may be regarded as linked amphibole chains rather than the symmetrical sheet structure of the next section.

The 'valency' oxygens are limited to one in each tetrahedron so the structure is based on $(\text{Si}_2\text{O}_5)^{2-}$ (see sheet structures, p. 125), rather than on the amphibole unit

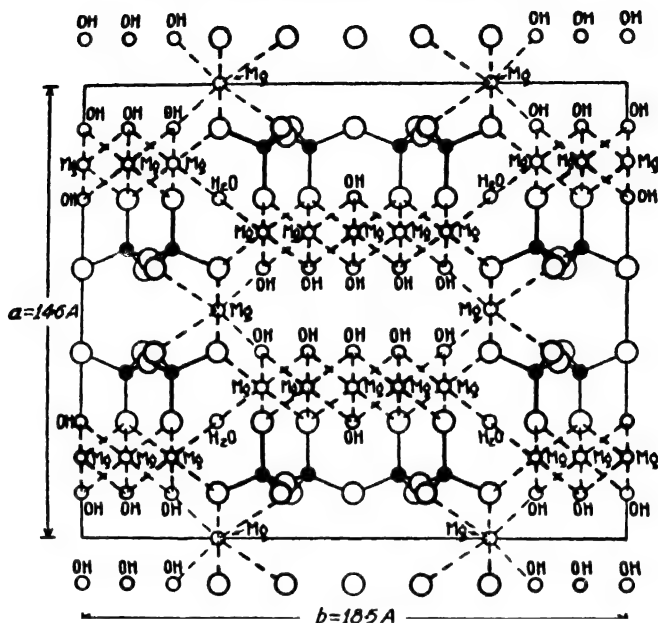


FIG. III.13. THE HYPOTHETICAL STRUCTURE OF PALYGORSKITE

(Si_4O_{11})⁶⁻. The linkages between chains in the vertical direction of the diagram are through extra cations of magnesium or aluminium which are in six-fold co-ordination with oxygen and hydroxyl units. A feature of the palygorskite structure is that series of holes are present which arise as a result of the alternating chain elements of the structure. Water molecules and, possibly, hydrated cations are contained in these channels, which resemble those of zeolite structures. Aluminium atoms replace silicon in tetrahedral co-ordination within the chains giving a unit composition which is complex. Bradley has suggested that the ideal chemical formula would be $\text{Si}_8\text{O}_{20}\text{Mg}_5(\text{OH})_2(\text{OH}_2)_4 \cdot 4\text{H}_2\text{O}$; which represented on a balanced layer concept would be $(\text{Si}_2\text{O}_5)_4^{8-}(\text{Mg}_5(\text{OH})_2)^{8+}(\text{OH}_2)_4 \cdot 4\text{H}_2\text{O}$, i.e. units of $(\text{Mg}_5(\text{OH})_2)^{8+}$ linking $n(\text{Si}_2\text{O}_5)^{2-}$ sheets.

The concept of the two sets of water molecules arises as a result of dehydration studies, which indicate that two molecules per unit are held more firmly than the others. It is suggested that these are directly linked to the cations which connect silica sheets as indicated in the diagram.

The structural constants of palygorskite are

Palygorskite (Attapulgite)

Space Group: C2/m

$Z = 2$

System: Pseudo-orthorhombic

Axes:

$a \sin \beta = 12.9 \text{ \AA}$

$b = 18.0 \text{ \AA}$

$c = 5.3 \text{ \AA}$

The mineral *sepiolite*¹ is similar and is again ideally a hydrated magnesium silicate. In appearance it is more spongy than palygorskite and is of more common occurrence. Sepiolite is an alteration product of serpentine and is often associated with limestones, particularly those of lacustrine origin. *Mountain cork* is thought to be a variety of sepiolite.

Sepiolite gives a similar X-ray line-pattern to that of palygorskite, therefore it is presumed that amphibole units are present. Although there have been several suggestions for alternative structural formulæ there appears to be no reason why the ideal palygorskite representation should not be applied. In fact the formula $\text{Si}_8\text{O}_{20}\text{Mg}_5(\text{OH})_2\text{OH}_2$ better describes sepiolite than palygorskite, for the latter always contains a comparatively large amount of substituted cations.

4. LAYER LATTICE STRUCTURES

WHEN three oxygen atoms of each silica tetrahedron (SiO_4)⁴⁻ are linked to similar units, a continuous sheet structure is formed. One oxygen only of each group of four is not fully satisfied electrically and requires to be linked to external cations. The sheet of silicon-oxygen atoms is capable of indefinite extension in two dimensions at right angles, therefore mineral structures within this group are invariably platy.

In most structures, the silica units are arranged in the form of hexagonal rings and the sheet is constructed of such symmetrical rings surrounded by six similar ones, each of which share two corners.

The construction of the hexagonal rings is important and in many structures the form is still not established with certainty. Each tetrahedral unit in the hexagonal ring is linked to others through an oxygen atom. The —Si—O—Si— bond angle can vary and thereby give rise to different ring formations. The two extremes are when the angle is $141^\circ 34'$ and when it is 180° . In the first case, a ring can be constructed where each silicon atom is at the same level above a zero plane and the valency oxygens all point vertically upwards. In the second case there are two possibilities: (a) every alternate valency oxygen points in opposite directions and the silicon atoms are on two levels; this is termed the 'rocking chair' or trans-form; and (b) the valency oxygens point in many directions and the silicon atoms are on three levels giving the so-called 'boat' or cis-form.

The majority of sheet structures are based on the concept that the Si—O—Si bond angle is about $141^\circ 34'$ but alternative structures are suggested, based on an angle of 180° , for montmorillonites. Ring structures of the trans-form occur in framework silicates but the cis-form of ring is not known, although it is common in organic chemistry.

Unlike all silicates which have so far been considered, sheet structures do not build up an extensive three-dimensional network by the simple link-up of silicon-oxygen units through additional cations. Definite layers are formed which are stacked one above another, and the bonds between each layer are relatively weak. Such minerals can, therefore, be sheared with comparative ease, and the crystal form is invariably plate-like.

¹ Longchambon, H., *Bull. Soc. Franc. Min.*, 60, 232, 1937.

Each mineral layer or plate is an independent unit, so Pauling's rules must be applied within each sheet. The layers must each be electrically balanced and each cation co-ordinated with anions in a way dependent on their size ratio. In some cases, the layers are not electrically balanced within themselves, so additional ions have to be absorbed on the surface of the layers.

Sheet structures can be simple where layers of tetrahedral silica units are linked to cations of one type with a specific co-ordination, or they may be more complex with substitutions of many types.

The principles governing the structure of layer silicates were established by Pauling¹ following a detailed study of large mica flakes suitable for single crystal X-ray investigation. Similar lattice configurations have now been ascribed to most clay minerals and well-defined groups have been established.

Naturally-occurring clays are usually composed of an admixture of many minerals. Quartz and other crystal forms are present, but, in addition, there is always a hydrated silicate of aluminium, magnesium or iron sometimes of small grain size. Such minerals are termed *clay minerals*, but the group also includes *micas*, *chlorites*, *serpentines* and other minerals, for these are similar in structure.

The simplest structure is that of the kaolin-type layer where the valency oxygen of a silica sheet is satisfied by one type of cation in octahedral co-ordination with oxygen or hydroxyl units. This is known as a single-layer structure because only one sheet of silicon-oxygen linkages is involved. Many minerals are examples of this class and this group has probably been studied more closely than any other silicate type.

SINGLE-LAYER GROUP

In general terms, the structure of this group is a series of layers, each with a sheet of linked silicon-oxygen tetrahedra, the excess valencies of which are satisfied by cations in octahedral co-ordination. The cations which can be contained in a group of six symmetrically-placed oxygen atoms are limited in numbers; there are in fact only four common ones, Al^{3+} , Fe^{3+} , Mg^{2+} and Fe^{2+} .

The valency contribution of a trivalent cation to each surrounding anion in six-fold co-ordination is one-half, whilst that of a divalent cation in a similar environment is only one-third. The lattice configuration of minerals which have trivalent cations must obviously be different from those which contain cations of lower charges. The single-layer minerals may, therefore, be further subdivided into structures with differently charged cations.

1. **Trivalent cations.** The important *kaolin*² group of minerals is based on layers of a single sheet of silicon-oxygen linkages bound through common anions to aluminium atoms arranged as in a gibbsite sheet and surrounded by six anions of oxygen and hydroxyl units.

Kaolinite is the name given to a specific mineral which is found in certain localities and has certain properties which enable it to be distinguished from others. *Cornish china clay* is composed largely of kaolinite which has been freed from

¹ Pauling, L., *Proc. Nat. Acad. Sci.*, 16, 123, 1930.

² The Clay Minerals Group of the Mineralogical Society has proposed the term *kandites* as a general name for kaolin group minerals.

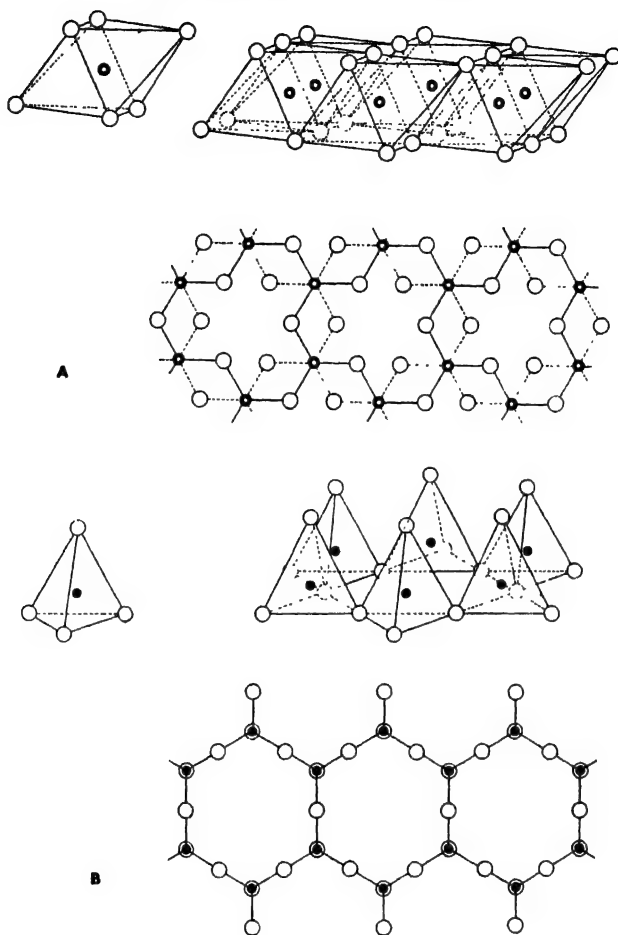


FIG. III.14. THE STRUCTURE OF A KAOLIN LAYER

- (A) The gibbsite unit showing an octahedral $\text{Al}(\text{OH})_3$ unit and the planar construction from side and top elevations;
 (B) the silica plane showing a tetrahedral unit and the planar construction from side and top projections

impurities of micaceous, felspathic and quartzitic types. Several other minerals have been isolated which are identical in chemical composition, yet are different from kaolinite in properties and structure. These minerals include *nacrite*, *dickite*, *livesite*, *halloysite*, *anauxite* and possibly *allophane*.

Nacrite and *dickite* are not common, although the latter is occasionally found in ironstone beds as a white powder in cavities and at the centre of nodules. Both *nacrite* and *dickite* are more coarsely crystalline than other kaolin minerals.

Livesite is probably the commonest kaolin mineral as it is associated with many

sedimentary clays. *Fireclays*, certain *bond-clays*, many *brick-earths* and some *ball-clays* are rich in *livesite* which is present as a finely-grained component, thereby endowing plasticity or stickiness to the clay.

Halloysite is a commonly-occurring kaolin mineral but is rare in the British Isles. Like kaolinite itself, halloysite is thought to be of hydrothermal origin.

Anauxite contains less aluminium than kaolinite yet has all the other characteristics of a kaolin group member—it is probably not common.

Allophane also differs from kaolinite in composition. It is a finely-grained mineral rather like an amorphous mixture of colloidal silica and alumina and may be a constituent of some sedimentary clays.

All kaolin minerals are composed of identical layers of composition $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, and differ only in the way in which these layers are arranged relative to each other. The fundamental unit consists of a kaolin layer, based on a hexagonal *silica network* (Fig. III.14B) which is linked to a layer of aluminium atoms through common oxygen linkages.

Aluminium hydroxide or *gibbsite*, $\text{Al}(\text{OH})_3$, has also a layer structure (Fig. III.14A) and the kaolin layer is essentially such a gibbsite layer condensed on the hexagonal silica-sheet. As the valency contribution of each aluminium ion to each co-ordinating anion is one-half, the 'valency' oxygens of the silica sheet, which all point vertically upwards, have to be linked to two aluminium atoms. Each oxygen atom thus receives one valency-share from a silicon and half from each of two aluminium ions and is electrically satisfied. Each aluminium ion is co-ordinated with three oxygen atoms linked to silicon atoms and to three hydroxyl units, one of which is on the same plane as the 'valency' oxygens and the other two are at a higher level.

The structure of kaolinite viewed from the side is shown in Fig. III.15A. The lowest plane in the layer is of oxygens linking adjacent silicons in the sheet above; then comes a layer of close-packed anions with a hydroxyl unit $(\text{OH})^-$ at the centre of six oxygen atoms. The next layer is of aluminium atoms, above which is a sheet of close-packed hydroxyl ions. As hydroxyl units are similar in size to oxygen atoms and all anions are relatively much larger than the cations, the layer structure can be imagined ideally as a close-packed system of spheres.

The thickness of the layer is 4.31 Å and the height of each plane is given in the diagram. The aluminium atoms are not situated directly above each 'valency' oxygen of the silica sheet, otherwise the structure would not be electrically balanced. The positions of aluminium atoms can be more clearly seen in Fig. III.15B, which is a diagrammatic representation looking downwards on to a layer.

Two aluminium atoms lie immediately above each hexagonal ring of silicon atoms. There are, however, three possible positions over each ring where octahedrally co-ordinated cations could fit, but if each were filled with trivalent cations the structure could not be electrically neutral. Only two-thirds of the available cationic positions are filled in the kaolin layer so the structure is termed *dioctahedral*.

The chemical representation of a kaolin layer is $(\text{Si}_2\text{O}_5)_n\text{Al}_2(\text{OH})_4$ implying sheets of $n(\text{Si}_2\text{O}_5)^{2-}$ linked to $(\text{Al}_2(\text{OH})_4)^{2+}$ units. This unit is of indefinite length in two directions along the *a* and *b* crystallographic axes.

Kaolin minerals form crystals which must contain many layers of this type stacked above each other and thereby giving extension along the *c*-axis. The

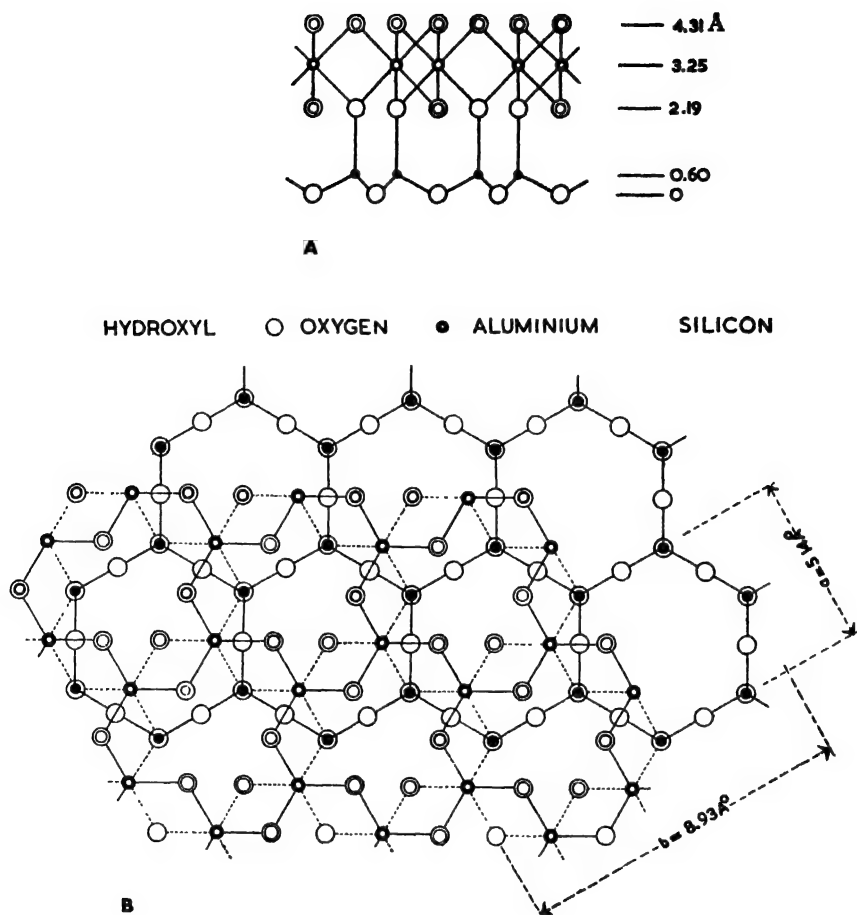


FIG. 111.15

(A) The kaolin layer (side elevation); (B) the kaolin layer (top elevation).

polymorphism in the kaolin minerals is related to the disposition of layers with respect to each other.

The forces which bind successive kaolin layers together are not known with certainty. As the layers are electrically neutral there can be no electrostatic or covalent bonding and although some authors have suggested that hydrogen bonds may be present between the hydroxyl sheet of one layer and the oxygen sheet of the next, this is now known to be incorrect. It is most probable that Van der Waal forces (see p. 73) are present and these serve to hold the layers together.

As successive kaolin sheets are in close contact with each other, it is to be expected that a particular relative disposition (or dispositions) will be more stable

than others. Hendricks¹ has suggested a simple arrangement, which also explains the relationship between the kaolin minerals.

A stable configuration is formed when the OH-groups on the top of one kaolin layer are 'paired' with oxygens in the lowest sheet of the unit immediately above as shown in Fig. III.16. This symmetrical arrangement can result only if one layer is placed upon another in a limited number of ways. For example, if one unit is arranged above another so that equivalent atoms lie immediately above each other, then the relationship of OH to O groups in successive layers will be as illustrated. The *c*-direction in the resulting structure will then be at right angles to the basal section and the crystallographic angle $\alpha = \beta = 90^\circ$.

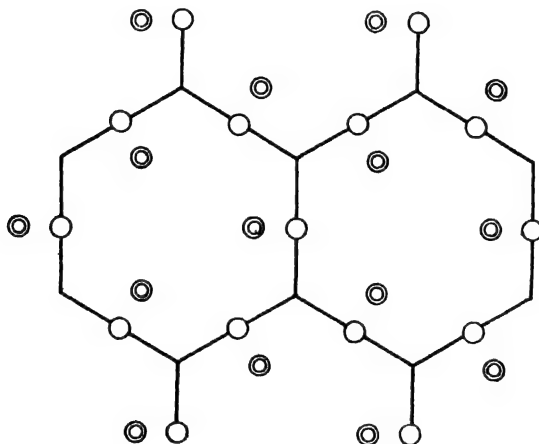


FIG. III.16. THE STABLE ARRANGEMENT OF OH GROUPS AND O ATOMS IN SUCCESSIVE LAYERS OF KAOLIN MINERALS

Certain displacements of one layer relative to another can also result in a stable arrangement of O—(OH) linking. For example, if the hexagonal rings of oxygen atoms are moved to the right along the *a*-axis by one-third of the *a*-dimension, a stable arrangement again results. Crystallographically, there has been a movement of $-a/3$ and the *c*-axis will now be inclined at an angle of $103^\circ 30'$ to the *a*-direction, so the angle β is no longer 90° . Starting once again with the shift of $-a/3$, a further movement of the hexagonal network in the *b*-direction produces the stable configuration for a shift of $+b/3$ or $-b/3$. The *c*-axis, or the line joining similar atoms in successive layers, will now not be at 90° with either the *a*- or *b*-directions. The angles can be calculated from simple geometrical considerations as $\alpha = 112^\circ 36'$ (when the shift is $-b/3$) and $78^\circ 42'$ (when $+b/3$); β is $103^\circ 30'$ in both cases.

With the aid of tracing paper the reader can work out the possible shifts along the *a*- and *b*-directions which will give the 'paired' O—(OH) configuration.

The total possible displacements are given in Table III.V.

¹ Hendricks, S. B., *Zeit. Krist.*, 100, 509, 1938.

TABLE III—V. POSSIBLE DISPLACEMENTS
OF SUCCESSIVE KAOLIN LAYERS WHICH GIVE THE HENDRICKS
STABLE O—(OH) CONFIGURATION

Fractional shift along <i>a</i> -direction	β -angle	Fractional shift along <i>b</i> -direction:						
		$+\frac{1}{2}$	$+\frac{1}{4}$	$+\frac{1}{8}$	0	$-\frac{1}{8}$	$-\frac{1}{4}$	$-\frac{1}{2}$
		α -angle:						
		56° 06'	67° 24'	78° 42'	90°	101° 18'	112° 36'	123° 54'
$+\frac{1}{2}$	69° 42'	✓	—	✓	—	✓	—	✓
$+\frac{1}{4}$	76° 30'	—	—	—	—	—	—	—
$+\frac{1}{8}$	83° 12'	✓	—	✓	—	✓	—	✓
0	90°	—	✓	—	✓	—	✓	—
$-\frac{1}{8}$	96° 48'	—	—	—	—	—	—	—
$-\frac{1}{4}$	103° 30'	—	✓	—	✓	—	✓	—
$-\frac{1}{2}$	110° 18'	✓	—	✓	—	✓	—	✓

The possible shifts which can give the stable configuration correspond to displacements in the *a*- and *b*-directions of multiples of $\pm \frac{1}{8}$.

When Hendricks first postulated this concept, the crystallographic details of the kaolin minerals were not as well known as they are now, as recent work has established the atomic configurations of several of the minerals with more precision. The structural schemes of the five main types of kaolin minerals are shown in Table III.VI.

TABLE III—VI. STRUCTURAL SCHEMES OF SOME KAOLIN MINERALS

Mineral	Crystal form	Crystallographic angles		
		α	β	γ
Nacrite*	Orthorhombic (monoclinic)	90°	90° 18'	90°
Dickite†	Monoclinic	90°	96° 48'	90°
Kaolinite‡	Triclinic	91° 48'	104° 30'	90°
Livesite (fireclay)§	Pseudo-monoclinic	(90°)	104° 30'	90°
Halloysite	Pseudo-hexagonal	(90°)	(90°)	90°

* Hendricks, S. B., *Zeit. Krist.*, 100, 509, 1938.

† Gruner, J. W., *Zeit. Krist.*, 83, 75 and 394, 1932.

‡ Brindley, G. W. and Robinson, K., *Min. Mag.*, 27, 242, 1946.

§ Brindley, G. W. and Robinson, K., *Trans. Brit. Ceram. Soc.*, 46, 49, 1947.

|| Brindley, G. W. and Robinson, K., *Min. Mag.*, 28, 393, 1948.

All these minerals have approximately the same chemical formula and differ chiefly in the arrangement of successive layers and not in the constitution of the layers themselves. They fit reasonably well into the scheme of possible structures suggested in Table III.V with the exception of dickite; the reason for this anomaly

will be shown later. Dickite falls into line in a way which demonstrates the correctness of Hendricks' assumption.

There is another complication which arises when kaolin layers are stacked above each other. There are only two aluminium atoms associated with each hexagonal silica ring, yet there are three possible positions into which they may be placed.

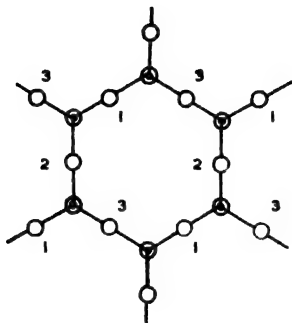


FIG. III.17. THE POSSIBLE RELATIVE POSITIONS OF ALUMINIUM ATOMS TO A SILICA HEXAGONAL RING IN THE KAOLIN LAYER

Fig. III.17 shows the hexagonal ring with the positions for two aluminium atoms. They may be at the points 1 and 2, or 1 and 3, or 2 and 3. In a single layer, all these combinations are identical, but when two successive layers are considered, the relative positions of the aluminium atoms influence the dimensions of the unit-cell. If, for example, one kaolin layer is placed immediately above another, the oxygen atoms in the lowest sheet of one layer are directly below similar ones in the top layer; silicon atoms in adjacent layers must also be along vertical lines for they are symmetrically arranged. Aluminium atoms need not be above one another, for in the lower layer they may be in the positions 1 and 2, but in the upper unit in any of the three alternatives 1-2, 1-3 or 2-3. Three or more layers provide additional complications.

The unit-cell dimensions in the c -direction will depend on the relative positions of aluminium atoms in successive layers.

The general structural character of the kaolin minerals is in accord with these principles. The unit layer is common to all, therefore it is not surprising that the a - and b -dimensions are very similar. The c -dimension is determined by the type of stacking of successive layers. Its angular relationship to the a - and b -axes depends on the relative displacement of the layers, and its length is governed by the arrangement of aluminium atoms in successive units.

Nacrite has kaolin layers arranged directly above one another, so the cell is virtually orthorhombic with $\alpha = \beta = \gamma = 90^\circ$. Hendricks¹ found that in practice β was $90^\circ 20' \pm 10'$, indicating a slight variance from orthorhombic symmetry. The length of the c -dimension is, however, 43 Å, so there must be six kaolin layers, for the separation between two is about 7.2 Å. The structural constants are:

¹ Loc. cit., p. 131.

Nacrite $\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$

Space Group: Cc

 $Z = 12$

System: Ortho. rhombic

Axes:

Angle:

 $a = 5.14 \text{ \AA}$ $b = 8.94 \quad (\beta = 90^\circ 20' \pm 10')$ $c = 4.43$

Dickite does not appear to conform to the stable arrangement of O-(OH) groups in successive layers.

Gruner¹ has carefully analysed the structural relationships in *dickite*. The β -angle (given as $96^\circ 48'$) could equally well be chosen as the complementary angle of $83^\circ 12'$ which would require a fractional displacement in the a -direction of $+\frac{1}{8}$ (see Table III.V). This alone would not explain the structure of *dickite*, because if it is to fit into one of the possible theoretical structures, there would have to be a shift of successive layers in the b -direction also. Pairing of O-(OH) units could occur for a movement of $\pm\frac{1}{2}$ and $\pm\frac{1}{8}$, resulting in an α -angle of $123^\circ 54'$, $101^\circ 18'$, $78^\circ 42'$ or $56^\circ 06'$. However the α -angle of *dickite* is close to 90° and does not correspond to any of the theoretically predicted ones. Gruner demonstrated by careful X-ray measurements that successive kaolin layers in *dickite* are in fact displaced in the b -direction, but this shift alternates between $+\frac{1}{8}$ and $-\frac{1}{8}$. The result is that the two displacements cancel out, giving an α -angle of 90° and a unit-cell length in the c -dimension equal to two layers (i.e. 14.3 \AA). This simplified concept does not account for all the features of the *dickite* structure, but is the one most generally accepted at the present time.

The structural constants of *dickite* are:

Dickite $\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$

Space Group: Cc

 $Z = 2$

System: Monoclinic

Axes:

Angle:

 $a = 5.14 \text{ \AA}$ $b = 8.94 \text{ \AA} \quad \beta = 83^\circ 40'$ $c = 14.42 \text{ \AA}$

Kaolinite. Gruner² analysed kaolinite in 1932 and deduced a monoclinic cell. The c -axis was inclined only in one direction to give a β -angle of about $104^\circ 30'$ corresponding to a displacement of layers in the a -direction of $-\frac{1}{8}$. More recent work by Brindley and Robinson³ has indicated that the unit-cell is really triclinic with $\alpha = 91^\circ 48'$. The c -dimension of 7.37 \AA indicates that there is only one layer per unit-cell.

The structure is illustrated in Fig. III.18 and the constants are

Kaolinite $\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$

Space Group: Cc

 $Z = 2$

System: Triclinic

Axes:

Angles:

 $a = 5.14 \text{ \AA}$ $b = 8.93 \text{ \AA}$ $c = 7.37 \text{ \AA}$ $\alpha = 91^\circ 48'$ $\beta = 104\frac{1}{2}^\circ - 105^\circ$ $\gamma = 90^\circ$ ¹ Loc. cit., p. 131.² Loc. cit., p. 131.³ Loc. cit., p. 131.

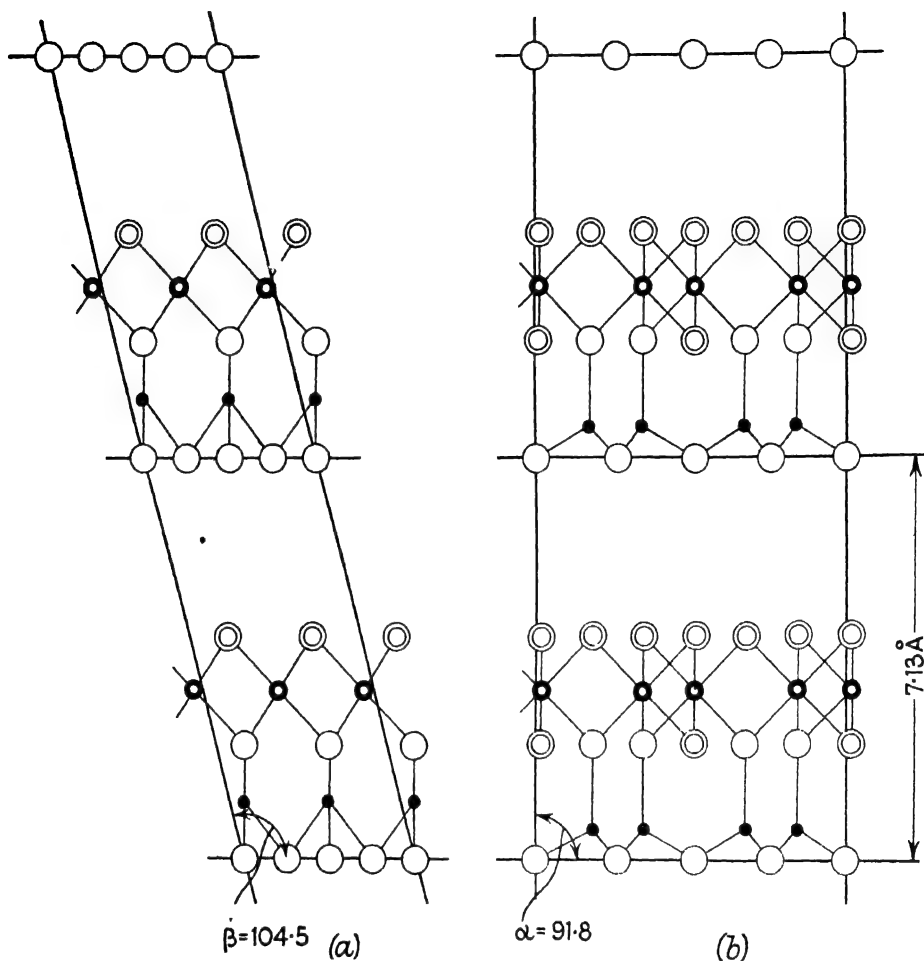


FIG. III.18. THE STRUCTURE OF KAOLINITE
 (a) Looking down the a -direction; and (b) looking down the b -direction.

Livesite. That a previously unrecognised kaolin mineral was present in fireclays and in some other sedimentary clays was first established by Grimshaw, Heaton and Roberts¹ using mainly thermal methods. The structure of this mineral has been deduced by Brindley and Robinson from X-ray measurements and they have suggested that the chief clay mineral in fireclays is intermediate between kaolinite and halloysite. The β -angle is 105° , which is near to that of kaolinite, but the α -angle is 90° , therefore the unit-cell is monoclinic. The displacements of layers along the a -direction are regular and equal to $-\frac{1}{3}$. The X-ray pattern indicates a high degree

¹ Grimshaw, R. W., Heaton, E., and Roberts, A. I., *Trans. British Ceramic Society*, 44, 20, 1945.

of disorder along the b -axis where layers are apparently randomly displaced by multiples of $\pm \frac{1}{3}$. The net result of considering several layers stacked upon each other is to give $\alpha = 90^\circ$.

Some of the lines in the X-ray diagram of the clay mineral from fireclays are banded, as in halloysite, and it has been suggested by Brindley and Robinson that a series of minerals exists with kaolinite as one extreme and meta-halloysite the other. Recent work carried out in the Ceramics Division at Leeds University on clay minerals purified from sedimentary clays has suggested that a mineral entity, livesite, exists with the kaolin formula. In all cases where it could be purified from associated kaolinite and hydrous mica, the X-ray patterns and thermal curves have been virtually identical. Hydrous mica is particularly difficult to eliminate, and, at a small particle size, it gives a diffuse pattern which complicates the powder diagram of pure livesite, and may explain the difference in banding in some samples. Livesite is inherently a fine-grained mineral and can be purified only by separation in a super-centrifuge. The ultimate crystallites are so minute that pure livesite gives a diffuse pattern thereby making structure analysis most difficult.

A feature of all samples of purified livesite from many localities has been the presence of a small amount of iron (1–2 per cent) which cannot be removed without disruption of the clay mineral. Chemical analysis suggests that it is in the ferrous state; it is not attributable to any known hydrate or oxide of iron. The clay mineral has a characteristic, pale yellow colour which turns faintly pink at about 450°C . If ferrous or ferric ions were contained in the crystal lattice of livesite, strains would be set up and the crystal size would be expected to be small.

Research at present in progress may establish the true structural arrangement of livesite and throw more light on its mode of formation.

Halloysite. Unlike the kaolin minerals previously described, halloysite exists in more than one form. The terminology applied to these varieties is not yet standardised. McEwan has proposed a nomenclature in which halloysite is retained as a general term and the particular form referred to as hydrated or dehydrated halloysite. The latter is commonly termed *metahalloysite*, although this may lead to confusion particularly among ceramists, for meta-kaolin has been defined as china clay which has lost its water of crystallisation. There seems to be no valid reason why the two forms should not simply be called (a) *hydrated halloysite* when the mineral with the high water content is implied, and (b) *normal halloysite* when referring to the type which resembles other members of the kaolin group in chemical composition.

Hydrated halloysite has the approximate composition $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$, i.e. two more molecules of water per unit of composition, whilst normal halloysite has the usual kaolinite formula. The hydrated variety has a basal spacing or distance between successive layers of 10.1 \AA which falls to 7.2 \AA on dehydration. Hendricks¹ has shown that the decrease of 2.9 \AA corresponds to a molecular sheet of water molecules and on this basis suggests that in hydrated halloysite an oriented layer of water is present between layers of kaolin.

Some natural deposits of halloysite are composed chiefly of the hydrated variety (Angleur halloysite is an example), other samples contain little, if any, and may have been dehydrated by natural processes. Grimshaw recently examined an

¹ Hendricks, S. B. and Jefferson, M. E., *Amer. Min.*, 23, 863, 1938.

American halloysite where two forms could be clearly recognised. A soft, easily water-dispersed portion gave a strong 10.1 Å X-ray line, whereas hard nodular pebbles were mainly the normal variety contaminated with trihydrate of alumina, gibbsite.

Hydrated halloysite changes to the normal form at about 50° C., but the basal spacing does not fall to 7.2 Å until the mineral is heated to about 400° C.

Normal halloysite, $\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$, has very complex stacking of successive kaolin layers, which are randomly displaced in the *a*- and *b*-crystallographic directions, although there is no reason to doubt that these displacements are multiples of $\pm \frac{1}{2}$ of the cell dimensions. There is no regular shift in either direction and the α and β angles are usually quoted as (90°).

Recent electron micrographs have proved that some halloysite crystals tend to roll up on themselves and form tubular shapes. In some way the layers must be strained, because the upper sheets of the layers are relatively smaller than the hexagonal network of silica, possibly because the aluminium atoms in the layers are not symmetrically placed as in a normal kaolin unit. Some atoms may be missing from one part of the layer and in other parts extra ones may be present; the resulting distortion would be sufficient to cause curvature.

Edelman and Favejee¹ have suggested that the layer units in hydrated halloysite are structurally different from those of kaolin. They visualise that every alternate silica tetrahedron in the sheet structure is inverted. More hydroxyl units are then incorporated into the structure and many other unusual features of halloysite are thereby explained. Similar structures have been proposed for minerals of the montmorillonite group; they are discussed more fully on p. 144.

Anauxite has a similar X-ray pattern to those of other kaolin minerals, yet its molecular ratio $\text{SiO}_2:\text{Al}_2\text{O}_3$ is 3:1 as against a normal 2:1. Hendricks² has suggested that anauxite may have a structure consisting of alternate layers of kaolin and neutral silica layers of composition $4\text{SiO}_2 \cdot \text{H}_2\text{O}$. If so, this silica unit would be of similar size to a kaolin layer, and the X-ray pattern would resemble that of a true kaolin mineral.

Allophane is classed as a kaolin mineral on rather inconclusive evidence. The molecular ratio of alumina to silica varies between 1:1 and 1:2, although it is usually about 1:1.5. The mineral appears amorphous and it gives no X-ray pattern. Grimshaw has analysed a sample from the south of England which had a molecular ratio of alumina to silica of 1:1.56; the differential thermal curve was quite characteristic and unlike a mixture of hydrated silica and alumina, which some authorities suggest allophane may be.

One feature of the kaolin minerals is the differences in their crystal sizes. Nacrite and dickite occur in comparatively large fragments, easily visible with an ordinary microscope; kaolinite crystals are much smaller and, for the most part, are only a few microns (1 micron = 10^{-4} cm.) in size; halloysite tubes are also small, very rarely larger than 1 micron; livesite is invariably in the form of smaller crystallites which are not perfectly resolved under magnifications of 35,000 times in the electron

¹ Edelman, C. H. and Favejee, J. C. L., *Zeit. Krist.*, 102, 417, 1940.

² Hendricks, S. B., *Jour. Geol.*, 50, 276, 1942.

microscope. These differences may be related to crystal structure or more particularly to the configuration along the *c*-dimension.

The stacking of kaolin layers may be compared to that in a pack of playing cards. Nacrite represents the state when each card lies directly above lower ones and a large structure can build up. Dickite is the condition where a progressively slight shift ($6-7^\circ$) is produced in one direction. Kaolinite is similar, but with a larger displacement ($14-15^\circ$) from the vertical in one direction. Livesite has displacements in two directions, randomly in one, regularly in the other; a pack of cards stacked in such fashion would be liable to collapse before many units could be added. Finally, the analogy of halloysite with random displacements in both directions could have little stability and would not be capable of great extension.

The thickness of the mineral plates undoubtedly influences the cross-sectional area of plate-like crystals. Unfortunately, detailed information of the thickness : size ratio for all kaolin minerals is not available but R. W. Grimshaw and T. E. Currie have examined dickite crystals under the microscope, and kaolinite and livesite by electron microscopy. In each, the ratio of the thickness of the crystal to the average length of its sides was closely similar and varied from 1:12 to 1:20.

Possibly all crystals which are composed of kaolin layers have maximum stability at a certain thickness : size ratio and each mineral can build up to a certain size, governed largely by the stability of stacking of the successive layers.

This description of the structural relationship between the kaolin minerals is of necessity brief; for more detailed information the reader is referred to a publication of the Mineralogical Society entitled *The X-ray Identification and Crystal Structures of Clay Minerals* under the editorship of G. W. Brindley. As the title suggests, methods of X-ray analysis for the identification of these and other minerals are also included.

Kaolin minerals must be one of the few silicate structures in which isomorphous substitution of cations is not extensive. This is all the more remarkable, because ferric iron can freely replace aluminium atoms in most structures (see pp. 114, 121, 143 etc.). It may be that a gibbsite layer just fits on to a hexagonal network of silica units and the introduction of ions of different sizes would be sufficient to distort the whole layer.

There have been reports, by numerous workers, of iron-bearing minerals similar to kaolin with ferric iron replacing aluminium, but these have not been substantiated by later work. *Faratsihite*, for example, was described as a basic hydrous silicate of aluminium and iron with the chemical composition $(\text{Al,Fe})_2\text{Si}_2\text{O}_5(\text{OH})_4$. It is a pale yellow mineral found in Madagascar and excited much attention until it was shown to be a mixture of kaolinite and nontronite.¹

At the present time there is no positive evidence of substitution in kaolin minerals, but there is no obvious reason why a small amount should not occur.

2. Divalent cations. Although the replacement of aluminium atoms in kaolinite with other trivalent cations is uncommon (even if it takes place at all), very similar structures with divalent ions are of frequent occurrence. Two important types are recognised, (*a*) those with magnesium and (*b*) those with ferrous iron as the

¹ Hendricks, S. B., *Amer. Min.*, 24, 529, 1939.

additional cation. Both structures are similar, for they are composed of layers stacked above one another in the c -dimension and held together by weak bonds.

The composition of a single layer is not unlike that of kaolin, because a silica hexagonal sheet unit is linked to cations in octahedral or six-fold co-ordination with oxygen and hydroxyl groups. Yet, as the cations are divalent, they donate to each surrounding anion only one-third of a valency-share. Therefore the valency-oxygens of each silica tetrahedron, which once again are all directed upwards, require

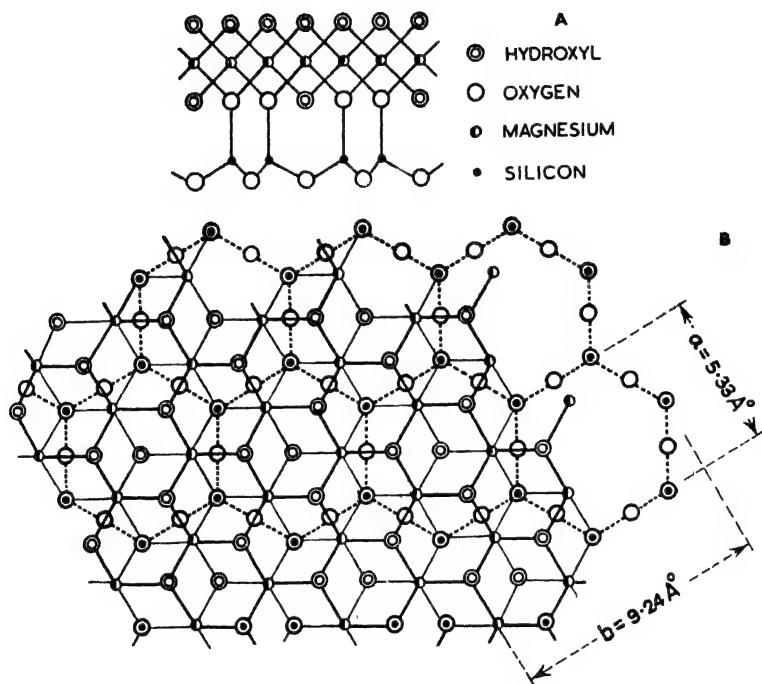


FIG. III.19. THE STRUCTURE OF ANTIGORITE
(A) Side elevation along the b -axis; (B) top elevation down the c -axis.

to be linked to three additional cations for valency satisfaction. Each hydroxyl group, of which there is one between each ring of six 'valency oxygens', and also a close-packed assembly forming the uppermost sheet of the layer structure, are linked to three divalent cations. To satisfy these requirements *three* cations must be placed symmetrically over each hexagonal ring of silicon atoms. By this means, all available octahedral positions are filled, whereas only two in every three are occupied by aluminium atoms in the kaolin structure. The minerals may be termed *trioctahedral*, to distinguish them from those in the dioctahedral kaolin series.

The composition of the unit layer is shown in Fig. III.19 A, B, and the diagram may be compared with that of kaolin in Fig. III.15.

Whereas the layer in kaolinite may be imagined as a gibbsite $(\text{Al}(\text{OH})_3)$ layer condensed on a sheet of hexagonally arranged silica units, so may the trioctahedral

minerals be visualised as a condensation of the corresponding hydroxide with a similar silica sheet. This is shown by comparing the kaolin unit with that of the magnesium- and iron-bearing analogue on the basis of their lattice dimensions.

Figs. III.15 and 19 show the diagrammatical representation of dioctahedral and trioctahedral layers and the hexagonal ring structure of the silica sheet beneath; arbitrary *a*- and *b*-directions are marked.

The ring structure of silica is common to all minerals and the dimensions of this unit can be calculated quite simply by assuming that the Si—O distance is 1.54 Å and that the Si—O—Si angle is 141° 34'. The length along *a* is 5.031 Å and along *b* is 8.715 Å. On to this unit a hydroxide layer has to be fitted, the *a*- and *b*-dimensions of which have been calculated for the three main types and are as follows:

Gibbsite Al(OH) ₃		Brucite Mg(OH) ₂		Ferrous hydroxide Fe(OH) ₂	
<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>
5.060 Å	8.624 Å	5.38 Å	9.33 Å	5.50 Å	9.72 Å

These figures, *a* and *b*, are not necessarily unit-cell dimensions of the hydroxides, but are chosen arbitrarily to fit over the hexagonal ring structure as illustrated in the diagram.

These *a*- and *b*-dimensions correspond to those of the unit-cell in the single-layer silicate minerals, and the effect of condensing different hydroxide structures with a silica sheet may be compared directly as in Table III.VII.

TABLE III—VII. COMPARISON OF THE DIMENSIONS OF THE HYDROXIDE LAYER AND CORRESPONDING LAYER SILICATE

	<i>Al mineral</i>		<i>Mg mineral</i>		<i>Fe²⁺ mineral</i>	
	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>
Hydroxide	5.06Å	8.62Å	5.38Å	9.33Å	5.50Å	9.72Å
Layer silicate	5.14Å	8.93Å	5.33Å	9.24Å	5.39Å	9.31Å

The ideal dimensions of the silica hexagonal network are *a* = 5.031 Å and *b* = 8.715 Å so that considerable distortion must take place if this sheet is to accommodate the magnesium and ferrous hydroxide layers.

(a) *Magnesium-bearing Minerals*

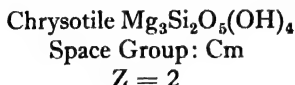
Minerals which contain magnesium ions in trioctahedral single-layer silicate structures are important in ceramic studies for they are present in serpentines and the more common forms of asbestos.

Two distinct mineral entities have been identified, *chrysotile* and *antigorite*, both of which are similar, being composed of unit layers of Mg₃Si₂O₅(OH)₄.

Chrysotile is a common constituent of asbestos minerals, and because of its fibrous nature it was thought to be an amphibole (see p. 122). However more recent

work by Warren and Hering¹ has established that the structure is really a layer-lattice very similar to that in the kaolin minerals.

The lattice distortion in the *b*-direction of the individual layers must be very great if a brucite layer is to fit over a silica network, and so the supposition that a considerable curvature occurs along this dimension is reasonable. The fibrous structure of chrysotile may be compared to the tubular form of halloysite where lattice distortion also results in curvature. Chrysotile crystals are capable of extension in the *a*-direction and long fibres result. Layers are stacked above one another, but in random fashion in one direction as in livesite. The structural constants are



System: Monoclinic
 Axes: Angle:
 $a = 5.33 \text{ \AA}$
 $b = 9.24$ $\beta = 93^\circ 16'$
 $c = 7.33$

Chrysotile is probably the most common form of asbestos; other types include tremolite, anthophyllite, etc., which are true amphiboles and have been mentioned in the appropriate section.

Antigorite is more complex because the *a*-dimension is 43.39 \AA (or $8 \times 5.42 \text{ \AA}$). Aruja² has suggested that it is due to a 'regular distortion' along this particular direction. The crystal habit is lamellar but the formula is essentially the same as chrysotile.

(b) *Iron-bearing Minerals*

Hydrated ferrous silicates are usually classified as *chlorites*, which are double-layer minerals to be described in the next section. Brindley³ has, however, shown that some chlorites, particularly those of the variety known as *chamosite*, have a single-layer construction rather like that of antigorite or chrysotile.

Chamosites are minerals which are common in the ironstone deposits associated with many of the Coal Measures and in some Irish (Antrim) bauxites. There are no reports of such minerals being found in associated fireclays, but some chlorites give X-ray powder diagrams strongly resembling that of livesite, which suggests that the stacking of layers is somewhat similar.

Antigorite-like *chamosites* appear to be of two forms, one of which has a monoclinic unit-cell (cf. livesite, p. 134) and the other with an orthorhombic cell suggesting a high degree of symmetry in the stacking of successive layers.

Apparently magnesium atoms can replace ferrous iron in the *chamosite* lattice as some samples contain appreciable proportions.

Another iron-bearing mineral based on a single-layer lattice is *cronstedtite* which ideally is $2\text{FeO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$. Hendricks⁴ suggests that this mineral has ferric iron replacing silicon in the hexagonal network and that the trioctahedral positions are filled with Fe^{2+} , Fe^{3+} and Al atoms. The full structural representation is, therefore, $(\text{Fe}^{3+}, \text{Fe}^{2+}, \text{Al}, \text{Ca})(\text{Fe}^{3+}\text{SiO}_4)(\text{OH})_5$. The replacement of a silicon by

¹ Warren, B. E. and Hering, K. W., *Phys. Rev.*, **59**, 925, 1941.

² Aruja, E., *Min. Mag.*, **27**, 65, 1945.

³ Brindley, G. W., *Min. Mag.*, **29**, 502, 1951.

⁴ Hendricks, S. B., *Amer. Min.*, **24**, 529, 1939.

a ferric ion must result in the substitution of a hydroxyl unit for an oxygen atom to balance valencies.

Amesite is another mineral based on antigorite, but with aluminium ions replacing silicon. Magnesium and ferrous ions fill the octahedral positions and some aluminium atoms are also present.

DOUBLE-LAYER FORMATION

WHEN a hydroxide layer such as *gibbsite* is condensed on a hexagonal silica network, a single-layer structure is formed. Gibbsite (also brucite and ferrous-hydroxide) layers consist of two sheets of hydroxyl units with linking cations; the top sheet is similar to the bottom one and there can be condensation of a further silica network, thereby completing a sandwich structure of two hexagonal silica units with a gibbsite layer between. The structure is capable of indefinite extension in two dimensions by covalent/ionic linkages.

This type of unit is illustrated in Fig. III.20. The uppermost silica network is displaced relative to the lower and the unit layer is bounded by two sheets of close-packed oxygen atoms.

When aluminium ions are present, only two out of three of the octahedral lattice sites are filled. The result is a dioctahedral double-layer structure and this fundamental unit is called the *pyrophyllite layer*. Expressed chemically the ideal formula of this unit is $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$ or structurally $\text{Al}_2(\text{Si}_2\text{O}_5)_2(\text{OH})_2$.

There is also a trioctahedral series when magnesium, iron or other divalent cations replace aluminium and the structure is equivalent to a further silica hexagonal network condensed on the single-layer structure of antigorite. This unit is termed a *talc layer* and has the chemical formula $3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$ or, structurally, $\text{Mg}_3(\text{Si}_2\text{O}_5)_2(\text{OH})_2$; it is shown in Fig. III.20.

Both pyrophyllite and talc layers are electrically balanced as can be seen by collecting the cationic and anionic charges together thus:

Pyrophyllite	Al_2^{3+}	Si_4^{4+}	O_{10}^{2-}	$(\text{OH})_2^{1-}$
	+6	+16	-20	-2
charge	<hr/>		<hr/>	
	+22		-22	
Talc	Mg_3^{2+}	Si_4^{4+}	O_{10}^{2-}	$(\text{OH})_2^{1-}$
	+6	+16	-20	-2
charge	<hr/>		<hr/>	
	+22		-22	

Many minerals are based on one or other of these basic structures, some of which are of great value in raw and fired ceramic materials. In addition to the minerals pyrophyllite and talc, the montmorillonites, micas, hydromicas, chlorites and vermiculites are all slight variants of the same basic structures.

Pyrophyllite. The mineral pyrophyllite, $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$, is used in ceramics particularly in the tile-making and the electrical porcelain (insulator) industries. It

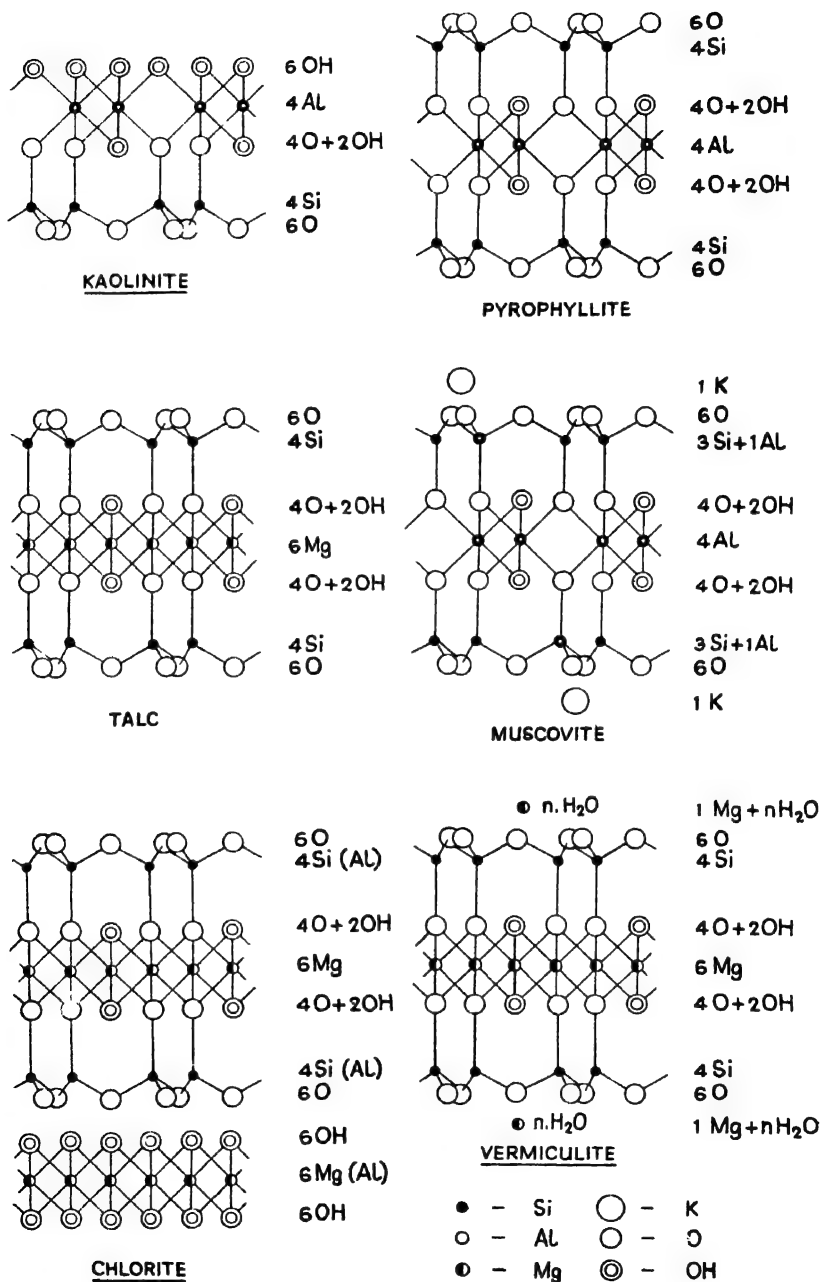


FIG. III.20. THE STRUCTURES OF SOME LAYER LATTICE MINERALS

occurs in many localities in small quantities, but the largest-known deposits are in the Piedmont area of North Carolina, U.S.A.

The unit layer of pyrophyllite has been described; the crystals of the mineral are built up by the stacking of such layers above one another. The forces holding adjacent layers together are not fully understood, but they are thought to be largely Van der Waal linkages (see p. 73).

The stacking of layers appears to be entirely random with an interplanar spacing or *c*-dimension of 9.3 Å.

Talc is another valuable ceramic mineral which is also known as *steatite*. Talc is the major component of soapstone and of most commercial steatites. Finely ground talc is well known as a cosmetic powder. Talc is also known as *French chalk* and as a component of refractories and ceramic insulators; when mixed with clay bodies and fired, talc yields cordierite or clinoenstatite, which are valued for their low expansion and insulating properties.

Structurally, talc is similar to pyrophyllite. Layers of the mineral are held together by Van der Waal forces and random stacking results. The distance between layers, or the basal spacing, is about 9.6 Å. The lattice constants¹ are:

Pyrophyllite		System: Monoclinic	Talc	
$\text{Al}_2(\text{Si}_2\text{O}_5)_2(\text{OH})_2$		Space Group: C2/c	$\text{Mg}_3(\text{Si}_2\text{O}_5)_2(\text{OH})_2$	
Axes:	Angle:	$Z = 4$	Axes:	Angle:
$a = 5.24 \text{ Å}$			$a = 5.26 \text{ Å}$	
$b = 8.90$	$\beta = 99^\circ 55'$		$b = 9.10 \text{ Å}$	$\beta = 100^\circ$
$c = 18.55$			$c = 18.81 \text{ Å}$	

Montmorillonite Minerals.² *Montmorillonite* is the name given to a clay mineral found near Montmorillon in France as long ago as 1874. Essentially it had the composition $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O} + x\text{H}_2\text{O}$ and was of exceptional stickiness. Many other minerals of similar properties yet with widely differing chemical composition have since been discovered.

X-ray analyses have established the structural similarities and it is now known that extensive substitution and replacements can take place within the lattice.

A wide range of minerals exists which might be included in the 'montmorillonite group', but the term *montmorillonite* now has a more restricted meaning, and implies a compound which is essentially a hydrated alumino-silicate with only little substitution.

Many clays which contain montmorillonite type minerals have been termed *bentonite*. This name has become common usage for commercial grades of montmorillonites.

The proposed structure of all minerals of the montmorillonite group is based on that of pyrophyllite or talc, but with the essential difference that the unit layers are not electrically neutral.

Montmorillonites have the property of absorbing cations and holding them strongly. As cations are positively charged it is assumed that the layers have a net

¹ Gruner, J. W., *Zeit. Krist.*, 88, 412, 1934.

² The Clay Minerals Group of the Mineralogical Society has proposed the terms *smectites* as a general name for montmorillonite group members.

negative charge, the result of ionic replacements within the lattice. Thus, the replacement of an Al^{3+} by a Mg^{2+} cation in octahedral co-ordination creates a unit deficiency of charge. In the mineral montmorillonite itself magnesium appears to replace aluminium in the approximate ratio of 1 to 6 and in other minerals of the montmorillonite group ferrous ions can replace, and aluminium (Al^{3+}) can take the place of, silicon (Si^{4+}) in the hexagonal network. The atoms in successive sheets of a layer are arranged as follows. Pyrophyllite is included for comparison.

TABLE III—VIII. THE ATOMIC ARRANGEMENT
IN SUCCESSIVE SHEETS OF MONTMORILLONITE AND
PYROPHYLLITE LAYERS

<i>Montmorillonite</i>	<i>Net charge</i>	<i>Pyrophyllite</i>	<i>Net charge</i>
3 O^{2-}	-6	3 O^{2-}	-6
2 Si^{4+}	+8	2 Si^{4+}	+8
2 $\text{O}^{2-} + (\text{OH})^{1-}$	-5	2 $\text{O}^{2-} + (\text{OH})^{1-}$	-5
1.67 $\text{Al}^{3+} + 0.33 \text{ Mg}^{2+}$	+5.67	2 Al^{3+}	+6
2 $\text{O}^{2-} + (\text{OH})^{1-}$	-5	2 $\text{O}^{2-} + (\text{OH})^{1-}$	-5
2 Si^{4+}	+8	2 Si^{4+}	+8
3 O^{2-}	-6	3 O^{2-}	-6
Sum of positive charges = 21.67		Sum of positive charges = 22	
Sum of negative charges = 22		Sum of negative charges = 22	

In all other respects, the structure of pyrophyllite shown in Fig. III.20 is indicative of montmorillonite. (Fig. III.21a.)

These are the views of such eminent authorities as Hofmann, Endell, Wilm, Maegdefrau, Marshall and Hendricks¹ who have all made important contributions to the structural relationships of montmorillonite minerals. There is also an alternative structure, proposed by Edelman and Favejee² which is claimed to account for certain properties of montmorillonites unexplained by the pyrophyllite analogy, and a similar structure is suggested for halloysite. They conceive that the silica hexagonal network is based on one of the alternative arrangements (p. 125) where the Si—O—Si bond angle is 180° and the rings are of the 'rocking chair' or *trans*-form, so that three alternate valency-oxygens point upwards and the other three downwards. Two of these sheets are linked to a gibbsite unit as illustrated in Fig. III.21b. Hydroxyl units project outwards from each layer and it is alleged that these behave as true hydroxide units and can combine with cations (M) to form O—M groupings. Other adsorption properties can be explained in a similar manner. The interesting feature of the Edelman and Favejee concept of montmorillonite is that the layers are electrically neutral and isomorphous replacements resulting in a charge-deficiency are not needed to account for the cationic adsorption. The layer may be represented as sheets composed as follows:

¹ (a) Hofmann, U., Endell, K. and Wilm, K., *Zeit. Krist.*, 86, 340, 1933; (b) Marshall, C. E., *Zeit. Krist.*, 91, 433, 1935; (c) Maegdefrau, E. and Hofmann, U., *Zeit. Krist.*, 98, 299, 1937; (d) Hendricks, S. B., *Jour. Geol.*, 50, 276, 1942.

² Edelman, C. H. and Favejee, J. C. L., *Zeit. Krist.*, 102, 417, 1940.

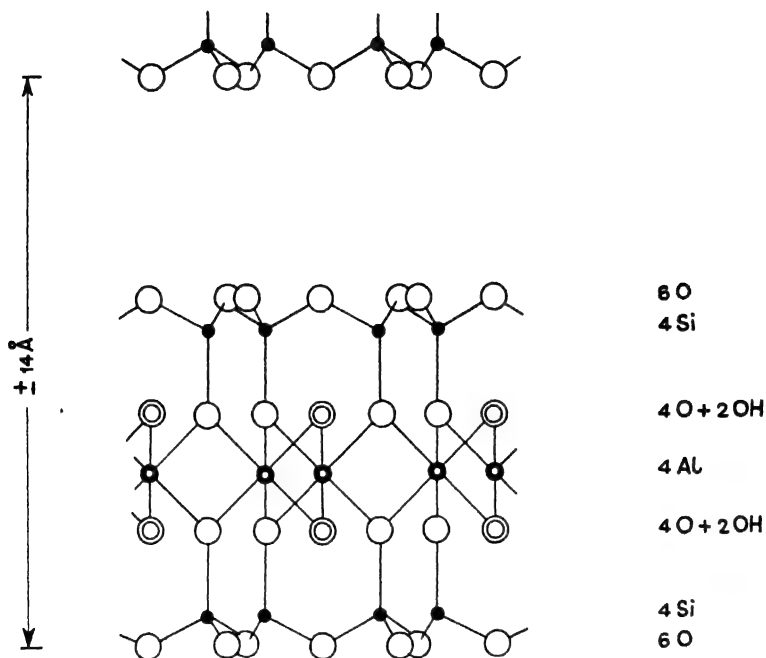


FIG. III.21(a). THE PROPOSED STRUCTURES FOR MONTMORILLONITE (IDEALISED)
(Hofmann, *et al.*)

1 (O—H) ¹⁻	net charge	-1	} Silica hexagonal ring unit (with -11 and +8 charges)
1 Si ⁴⁺	" "	+4	
3 O ²⁻	" "	-6	
1 Si ⁴⁺	" "	+4	
1 O ²⁻ + 2(OH) ¹⁻	" "	-4	
2 Al ³⁺	" "	+6	} Silica hexagonal ring unit
etc., in reverse order			
Sum of negative charges = 22			
Sum of positive charges = 22			

The resulting total formula is $\text{Si}_4\text{Al}_4\text{O}_8(\text{OH})_8(\text{O—H})_4$. This structure would give rise to a much higher cation-adsorption than would actually take place if all (O—H) groups were ionisable. For the formula to be correct it must be assumed that all the (O—H) ions are not dissociated or that the silica units in the hexagonal networks are not inverted regularly.¹

¹ Loc. cit., p. 144.

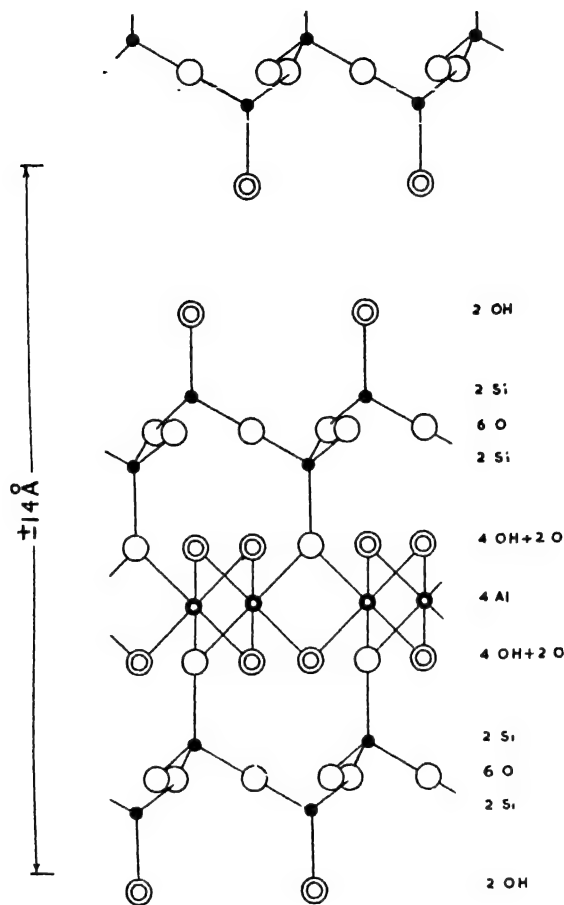
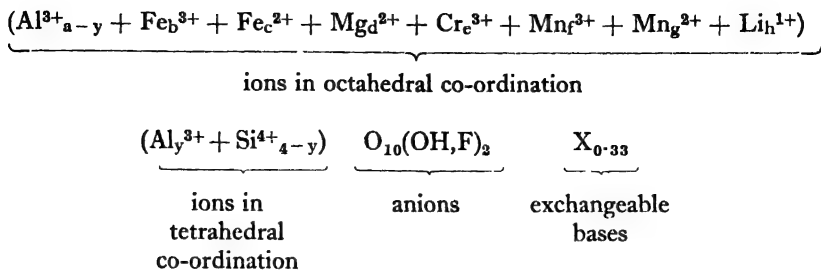


FIG. III.21(b). THE PROPOSED STRUCTURES FOR MONTMORILLONITE (IDEALISED)
(Edelman and Favejee)

Ross and Hendricks,¹ however, have accepted the structure based on pyrophyllite and have classified all the montmorillonite group members on this basis. Their ideas have met with fairly general approval, but the Edelman-Favejee concept has not been fully disproved.

In the course of a general survey of montmorillonite minerals from numerous localities, over 100 carefully selected samples have been analysed by Ross and Hendricks, who express the formula in the following general terms:

¹ Ross, C. S. and Hendricks, S. B., *U.S. Geol. Survey Prof. Paper*, No. 205-B.



This simply means that these minerals can have a variety of cations in octahedral positions, i.e. in the central hydroxide layer; and silicon and aluminium ions in tetrahedral positions in the hexagonal networks.

In deducing the structural formulæ from the chemical composition of the montmorillonite minerals, Ross and Hendricks made several assumptions. These include:

(a) That the sum of the charges of all the anions (namely oxygen and hydroxyl) always totals twenty-two in the unit formula; made up usually of ten divalent oxygen and two hydroxyl anions.

(b) That the number of cations in tetrahedral co-ordination (namely silicon and aluminium) always totals four.

(c) That the exchangeable cations counterbalance the charge deficiency on the layers. The actual determination of this value indicated that the figure was usually about 0.33 positive charge per unit formula, and Ross and Hendricks suggest that this value is constant for all minerals of this type.

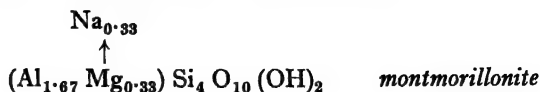
The calculated structural formulæ for the 105 samples of montmorillonites has clarified present-day knowledge of this mineral group, and shown that an apparently bewildering series can be very much simplified.

The number and type of cations in the octahedral layer can be calculated and on this basis alone there is a major distinction between the minerals of the montmorillonite group, because the number of cations in the central sheet was either between 2.00 and 2.22 or between 2.76 and 3.00. Both a *dioctahedral* and a *trioctahedral* series are thus clearly established.

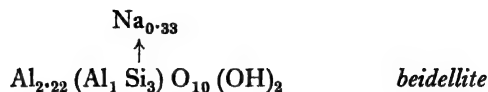
The amount of substitution in the silica (tetrahedral) layer and in the central (octahedral) layer of cations can be calculated and as a result it was established that montmorillonites form continuous series of minerals with end members which could be predicted with some certainty. Although many cations are present in the structure of montmorillonite minerals, those which occur in appreciable amounts are limited to silicon (Si^{4+}), aluminium (Al^{3+}), magnesium (Mg^{2+}), iron in the ferric (Fe^{3+}) and ferrous (Fe^{2+}) forms and lithium (Li^{1+}).

Of the 105 samples analysed by Ross and Hendricks no fewer than 54 fell within one group, the end members of which could be represented by the formulæ¹

¹ The exchangeable cation is usually represented in the formula, linked to the cationic group which is deficient in charge.



and



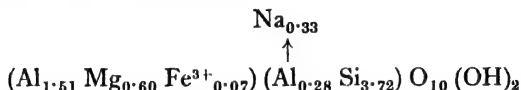
Small amounts of Fe^{3+} may be present in both the structures.

The former mineral is *montmorillonite*, the latter is *beidellite*, and a complete range of solid solutions exists between these two extremes.

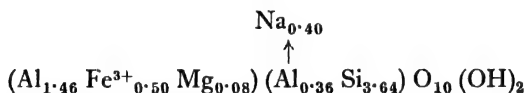
The number of cations in octahedral or six-fold co-ordination varies in this series between 2.00 and 2.22 so they are of the dioctahedral series.

Wyoming Bentonite is a member of the montmorillonite/beidellite series. Other examples of especial interest are:

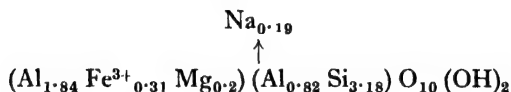
- (1) The *mineral from Montmorillon*, in France, which is



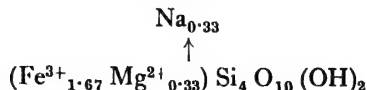
- (2) A *Beidellite* from Beidell, Colorado, is



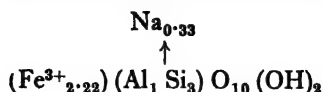
which is much closer to montmorillonite than to ideal beidellite in composition. The mineral which is closest to the beidellite extreme of all samples examined by Ross and Hendricks is from Roseland, Vancouver, and its analysis is



When a montmorillonite mineral is of the above type, i.e. when the sum of octahedral cations is between 2.00 and 2.22, and yet a considerable amount of iron is present, the mineral is termed *nontronite*. Ferric cations can replace aluminium in all proportions in the octahedral layer, so there is really a complete range of solid solutions between the end members montmorillonite, beidellite and nontronite. Nontronite has to be represented by two extreme type formulæ:



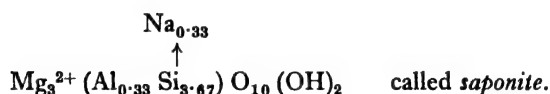
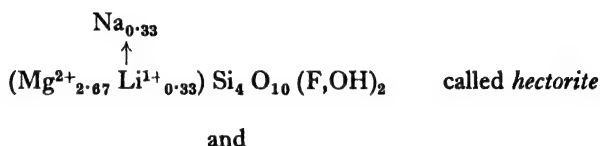
and



The former is not entirely suitable as no nontronites have been reported which contain so much magnesium, and the charge-deficiency is invariably centred mainly in the tetrahedral layer.

Of the remaining montmorillonite type minerals analysed by Ross and Hendricks a small number were entirely unrelated to the dioctahedral series. These minerals have structural formulæ where the sum of cations in octahedral positions is very nearly 3. Therefore the structure must be based on that of trioctahedral talc rather than on pyrophyllite which is the basis of the minerals of the montmorillonite-beidellite-nontronite group.

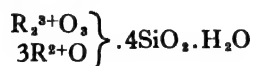
There is a series of minerals of the trioctahedral series with two end members represented by the formulæ



Apparently there is a complete range of solid solutions between these two extremes, but it is unlikely that dioctahedral and trioctahedral montmorillonite types form intermediate members.

In all the theoretical structures which have been represented, the exchangeable base has been given as sodium. This is not necessarily the natural form of the mineral, for other cations such as Ca^{2+} and K^+ may be adsorbed. The structural formula is not influenced in any way by the inclusion of other cations, but the properties of the mineral may be considerably affected.

Montmorillonite minerals are often expressed chemically as having the formula $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$. This can be misleading as the aluminium content may be very small as in nontronite or hectorite. It is not even accurate to express the formula as



because the molecular ratio of metallic oxide to silica may approach 1:2, as in beidellite, nontronite and saponite. Only in ideal montmorillonite is the oxide ratio about 1:4.

Montmorillonites are common clay minerals, though they occur in only a few places in the British Isles. The modes of formation are known to vary, but they are a frequent weathering product of volcanic glasses. Montmorillonites are often

associated with lacustrine or fresh-water lake clay deposits and may change to kaolin under prolonged leaching.

In the foregoing pages only the composition of the layers which make up the montmorillonites has been described; there remains the problem of extension in the c -dimension, i.e. the stacking of successive layers.

Alkali or alkaline earth cations which are absorbed by the layers in montmorillonites must play a large share in the linking of adjacent units. Such ions penetrate between the layers and, although not held firmly in any way, they probably form a bridge between two negatively-charged units.

Apparently, in montmorillonites, stacking of successive layers is completely random; some minerals are fibrous in habit, e.g. hectorite, suggesting that the layers may be distorted as in halloysite or chrysotile.

When montmorillonites are completely dried at temperatures of about 150°C ., the basal spacing, or distance between the lowest sheet of one layer and the equivalent sheet in the layer above, is about 11.0 \AA and varies with the size of adsorbed cation. When water is added, this spacing increases to about 14.0 \AA indicating that water has penetrated between the layers. As more water is introduced this spacing increases to 20 \AA or more and in a dilute montmorillonite suspension the individual plates are probably completely isolated. This theory has been substantiated by adsorption measurements¹ by which the surface area can be determined.

The mechanism of water adsorption by montmorillonites is still a matter for conjecture. There is conflicting evidence as to whether the basal spacing of montmorillonite increases uniformly with water adsorption, or whether the increase is step-wise, thus indicating the formation of hydrate layers round the cations. Experiments with minerals in which the adsorbed cations were Ca^{2+} or H^{+} showed, undoubtedly, a non-uniform increase² whilst Na^{+} -montmorillonites have a smooth expansion with increasing water content.³ This increase in the size of montmorillonite crystals on the addition of water is termed 'swelling' and has many important practical applications.

Montmorillonites are known to exhibit great plasticity, stickiness and strength in the wet and dry states. This is mainly due to the extremely large specific surface area which is exposed on dispersion in water.

In addition to their ability to absorb inorganic cations and water, montmorillonites are capable of taking up organic molecules in interlamellar positions. Large organic cations such as amines and proteins can replace the exchangeable balancing cations. Mono- and, sometimes, di-molecular layers are absorbed in this way depending on the size of cation and charge-deficiency in the layers. Organic liquids or solids may also be adsorbed where the mechanism is not attributable to base-exchange phenomena. Glycerols, resorcinol, catechol and pyrogallol are only a few examples and it was partly to explain the mechanism by which such compounds are held between montmorillonite plates that Edelman and Favejee postulated their

¹ Schofield, R. K., *Nature*, **160**, 408, 1947.

² Bradley, W. F., Grim, R. E. and Clark, W. L., *Zeit. Krist.*, **97**, 216, 1937.

³ Hofmann, U. and Bilke, N., *Koll. Zeit.*, **77**, 239, 1936.

Nagelschmidt, G., *Zeit. Krist.*, **93**, 481, 1936.

structural representation. Absorptions of this type are diagnostic in that montmorillonites are the only minerals which give a normal 14 Å X-ray spacing increased to about 18 Å by glycerol and some similar compounds.

Dyestuffs are also adsorbed by montmorillonites and, in some cases, this is of value in the microscopic examination of these fine-particled minerals. This topic will be discussed more fully in Chapter V. Fullers' earths, which are usually montmorillonites of one type (commonly *saponite*), are of particular importance in the paint industry, as a direct result of their ability to absorb colouring agents.

Mica Group. *Micas* may be regarded as naturally following the montmorillonites as their structure (Fig. III.20) is also based on those of pyrophyllite or talc. The layers are not electrically balanced and require the presence of extra cations in inter-lamellar positions.

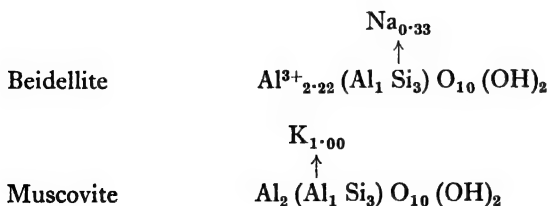
There is one important difference, however, which results in a fundamental change in the physical character. The layers in mica have a greater deficiency of charge and the balancing cations are held more strongly; in fact, there is ionic bonding, linking successive sheets through these additional cations. Unlike montmorillonite type minerals the layers of micas cannot be expanded by water, nor can the cations between them be exchanged or removed in any way other than by decomposition of the mineral.

Micas are primary igneous minerals; they crystallise in large platelike masses which are easily cleaved along their basal section. They were the first layer-lattice silicates to be examined by X-rays and their structure, as defined by Pauling,¹ has formed the basis for other minerals of similar layer construction.

Earlier workers were of the opinion that the essential difference between montmorillonite and the mica minerals was that whereas the former had its charge-deficiency in the central octahedral layer, the deficiency in micas was entirely in the outer tetrahedral networks. From this it is to be expected that the cations in micas would be held more firmly than those in the montmorillonite minerals.

Ross and Hendricks have shown, however, that beidellite has as much substitution in the tetrahedral layer as mica, yet it still retains the character of a montmorillonite. Beidellite does, however, demonstrate the essential difference between the two groups for, unlike minerals of the mica group, the charge-deficiency in the external sheets of the unit layers of beidellite is partly balanced by additional cations included in octahedral positions. The average net residual negative charge on a unit of montmorillonite is 0.33 whilst in mica it is about 1.00.

The essential difference between beidellite and muscovite mica is best expressed by their structural formulæ:



¹ Loc. cit., p. 126.

Potassium cations in muscovite are symmetrically placed over each hexagonal ring in the external sheets of the layers. In this way they are linked to six oxygen atoms of one sheet and six in the adjacent layer, making twelve in all. The interlayer distance is about 9.8 Å.

Micas are also of complex chemical composition being mainly hydrated alumino-silicates but always containing notable proportions of alkalis, alkaline earths, iron and, sometimes, fluorine.

The structural formula of a particular mica may be calculated from the chemical analysis as for montmorillonites. Within the mica group there is a further subdivision into a dioctahedral and trioctahedral series based on pyrophyllite and talc respectively.

Muscovite mica is a true dioctahedral mica and has the chemical composition $K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$.

One silicon atom in every four in the outermost tetrahedral positions of each layer is replaced by an aluminium atom, thereby causing a unit deficiency of charge. This is not a general rule, however, for isomorphous replacements in the octahedral layer may also cause at least part of the net negative charge.

There are three important groups of micas:

(a) A dioctahedral series when trivalent cations occupy the octahedral positions and the structure is based on pyrophyllite;

(b) A trioctahedral series, with trivalent and monovalent cations (Lithium Li^+) in octahedral positions;

(c) A normal trioctahedral series with divalent cations arranged as in talc.

Examples of each series are summarised in Table III.IX.¹

TABLE III—IX. THE MICA SERIES

Series	Mineral	Composition*
<i>Dioctahedral</i> Muscovite system	Muscovite Phengite Paragonite	$K_2(Al_4)(Al_2Si_6)O_{20}(OH)_4$ $K_2[(Mg^{2+}, Fe^{2+})Al_3](Al_1Si_7)O_{20}(OH)_4$ $Na_2(Al_4)(Al_2Si_6)O_{20}(OH)_4$
<i>Trioctahedral</i> Lepidolite system	Lepidolite Polyolithionite Protolithionite Zinnwaldite Phlogopite	$K_2(Li_3 + Al_3^{3+})(Al_2Si_6)O_{20}(OH, F)_4$ $K_2(Li_3 + Al_3^{3+})Si_6O_{20}(OH, F)_4$ $K_2(Li_3 + Fe_3^{2+} + Al_3^{3+})(Al_2Si_6)O_{20}(OH, F)_4$ $K_2(Li_3 + Fe_3^{2+} + Al_3^{3+})(Al_2Si_6)O_{20}(OH, F)_4$ $K_2(Mg_6)(Al_2Si_6)O_{20}(OH)_4$
Biotite system	Biotite Annite	$K_2[(Mg^{2+}, Fe^{2+})_3](Al_2Si_6)O_{20}(OH)_4$ $K_2(Fe^{2+})_6(Al_2Si_6)O_{20}(OH)_4$

* These compositions are ideal, as natural micas are complex in composition. Extensive solid solution occurs, but there is a sharp contrast between the dioctahedral and trioctahedral series.

¹ In this table the structural formulæ have been doubled to avoid fractional representation.

Winchell¹ has termed the two series *heptaphyllite* and *octaphyllite* on the basis of the number of cations per structural unit; thus *muscovite*, $\text{K Al}_2(\text{Al}.\text{Si}_3)\text{O}_{10}(\text{OH})_2$, has seven cations, whilst *phlogopite*, $\text{K Mg}_3(\text{Al}.\text{Si}_3)\text{O}_{10}(\text{OH})_2$, has eight. This terminology is common in mineralogical text-books but is not of such general application in other mineral groups.

The minerals in Table III.IX are called the *elastic* or true micas, but there is another type known as the *brittle* micas which are of similar composition. The distinguishing feature of the brittle type is that calcium or magnesium ions are always present as 'linking' or 'bridging' ions. The charge-deficiency lies mainly in the tetrahedral layer but it is usually greater than in true mica.

Three minerals *margarite*, *chloritoid* and *clintonite* are thought to belong to this group, but their structural relationships are still in doubt. *Margarite* is considered to be $\text{Ca Al}_2(\text{Al}_2\text{Si}_2)\text{O}_{10}(\text{OH})_2$; with every alternative silicon in the tetrahedral layer replaced by aluminium. There is extensive isomorphous replacement and solid solution.

The stacking of the successive layers in micas is of great complexity. Each cation linking successive sheets is in twelve-fold co-ordination with oxygens, six of which are part of the lower sheet of one layer and the other six are part of the upper sheet of the layer-unit below. There is a multiplicity of ways in which this arrangement can come about and, consequently, the polymorphism in micas is highly complex. This subject has been carefully analysed by Hendricks and Jefferson² who have shown that the unit-cell dimensions of many micas are exceptionally large along the c-dimension.

All the mica minerals are monoclinic, as a result of the non-symmetrical arrangement of the two silica sheets in each layer. The structural constants of muscovite are

Muscovite $\text{KAl}_2(\text{Al}.\text{Si}_3)\text{O}_{10}(\text{OH})_2$

System: Monoclinic

Space Group: C2/c

Axes:

Angle:

$Z = 4$ (normal)

$a = 5.18 \text{ \AA}$

$b = 9.02 \text{ \AA}$

$\beta = 95^\circ 30'$

$c = 20.04 \text{ \AA}$ (normal equivalent to two sheets)

The *elastic* or true micas have predominantly potassium cations linking successive sheets. Although the sodium mica, *paragonite*, has been described, Winchell considers that there is no conclusive evidence that such a mineral exists. Undoubtedly, micas which contain a high proportion of sodium are rare and this may be related to the spacial configuration within this mineral group. As sodium ions are smaller than potassium ions, the former may not be held quite as tightly between layers of mica units. If so, sodium micas would presumably not form so readily and would be more easily decomposed.

Hydrous Micas and Illites. In addition to the true micas of primary formations there is another type which is of secondary origin. Many micas are known in sedimentary clays which do not correspond in composition to the true micas. These

¹ Winchell, A. N., *Amer. Min.*, 13, 267, 1927.

Hendricks, S. B. and Jefferson, M. E., *Amer. Min.*, 24, 729, 1939.

secondary minerals consist of grains of variable size ranging from readily visible crystallites to particles of the same dimensions as the clay minerals—a range of 4 mm. or more to less than 0.005 mm.

These secondary micaceous minerals are of common occurrence in fireclays and some other clays and are the principal alkali-bearing constituents in them. It seems certain that many of these micas are secondary products and not formed by crystallisation from magmas. The larger-grained samples are most likely of *antigenic* origin, i.e. they are the result of a breakdown of true primary mica by weathering or chemical agencies. On the other hand, some of the finely-grained minerals may be *digenic*, i.e. synthesised from colloidal constituents by natural processes.

These secondary micas, though of general occurrence, are known by a variety of names and no standard terminology has yet been accepted.

The first specific name proposed for a mineral of the micaceous type, having only half the normal content of potassium, was *bravaisite*. This mineral has, however, been proved to be a mixture of montmorillonite and a micaceous mineral. The name *bravaisite* is, however, still retained by some authorities.

In 1937, Grim¹ proposed the general name *illite* for a group of mica-like minerals with less alkali ions than muscovite, of small particle size, having a 10 Å spacing and showing no expanding lattice characteristics. Maegdefrau and Hofmann² have termed similar minerals *glimmerartigen tonmineralen* or more simply *glimmerton*. Other mineralogists have adopted the name *hydrous mica* for larger-sized fragments which are common in sedimentary deposits and this is probably the best and most descriptive term for the whole group. These micaceous minerals are characterised by having a larger water-content together with a smaller amount of alkali than true micas. Another name which is in general use for this class of minerals is *sericite*.

In addition to this group-terminology, specific minerals have been described and named, e.g. *brammalite* which is a sodium-bearing hydrous mica.

Although the mineral group of hydrous micas is widely recognised, the structural relationships have not been fully elucidated. Finely-grained samples are invariably contaminated with impurities which are difficult to remove, and this makes the true composition of the mineral uncertain. Larger-sized flakes have been isolated³ in what appears to be a fairly pure state, but cracks and fissures may contain impurities which cannot be removed.

Typical chemical analyses of hydrous micas and illites are given in Table III.X; an analysis of true muscovite mica (No. 7) is included for comparison.

In general, the secondary micas contain less alkali and more water than true muscovite. All the minerals in the table are of the dioctahedral series, but it is probable that a trioctahedral series exists, based on biotite.

The mineral *glauconite*, which is a common constituent of marine clays, may also be classified as a hydrous mica or illite, with more iron than is usual.

There are large variations in the compositions of minerals in the hydrous mica or illite group. A wide range of minerals is probable with gradually decreasing

¹ Grim, R. E., Bray, R. M. and Bradley, W. F., *Amer. Min.*, 22, 813, 1937.

² Maegdefrau, E. and Hofmann, U., *Sprechsaal*, 74, 369, 1941.

³ Carr, K., Grimshaw, R. W. and Roberts, A. L., *Min. Mag.*, 30, 139, 1953.

Norrish and Brown¹ have suggested that hydroxonium ions (H_3O^+) replace potassium ions between the layers of muscovite and they have deduced structural formulæ on this basis. This is a not unreasonable supposition, for these two cations are of comparable sizes and such substitution is known in other mineralogical systems.

R. W. Grimshaw and A. G. Sadler have recently examined a wide range of hydrous micas from British fireclays. By careful sedimentation and heavy liquid separation, pure crystals have been extracted from many clays. The composition of these purified minerals is extremely variable in a way which is not apparently related to geological sequence. Differences of composition have been recorded not only from sample to sample, but within the grain-size range of minerals from one particular locality.

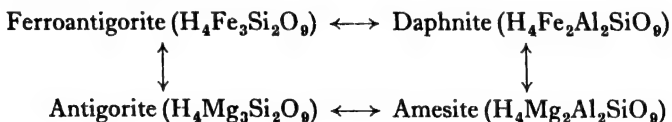
All minerals of the hydrous mica type have a structure very similar to muscovite mica. The unit-cell consists of two layers of ideal composition



but, in practice, with less potassium and more hydroxyl.

Chlorites. *Chlorites* form a class of platy minerals, occurring in many sedimentary deposits, which are similar to mica in appearance but much softer and of quite different compositions. Essentially they are hydrated silicates of magnesium and aluminium with a proportion of iron in either the ferrous or ferric form. The crystals, which are usually of small grain size, are greenish in colour whence the name *chlorites*. Some mineralogists term them '*flexible*' micas; they are extremely variable in composition.

Winchell considers that chlorites may be expressed as solid solutions of four end members which are:



Mauguin,² McMurchy³ and Brindley *et al.*⁴ have shown that some chloritic minerals have a characteristic structure which is not shared by antigorite and amesite (i.e. single-layer silicates). Their structure is based on that of *talc* but with a layer of *brucite*, $\text{Mg}(\text{OH})_2$, interposed between each talc layer. Isomorphous replacements are present in both layers; e.g. aluminium replaces silicon in the tetrahedral layers and aluminium may also be substituted for magnesium or ferrous ions in the octahedral positions. Ferric iron (Fe^{3+}) and chromium (Cr^{3+}) may also be present. As a result of such replacements the talc layers acquire a net *negative* charge (because of the substitution of Al^{3+} for Si^{4+}), which is balanced by a residual *positive* charge on the brucite layers (where Al^{3+} replaces Mg^{2+} ions). It is therefore probable that the bonding between all the layers is partly ionic in character.

¹ Norrish, K. and Brown, G., *Min. Mag.*, 29, 929, 1952.

² Mauguin, C. H., *C.R. Acad. Sci.*, 186, 1852, 1928.

³ McMurchy, R. C., *Zeit. Krist.*, 88, 420, 1934.

⁴ Brindley, G. W., Oughton, B. M. and Robinson, K., *Acta. Cryst.*, 3, 408, 1950.

The *stacking of layers* in the *c*-dimension is complex and many units may be involved. The separation between equivalent sheets of atoms in successive planes in this direction is 14.2 Å. The structural constants of a typical chlorite, *penninite*, are

Penninite—approx. $\text{Al}_2\text{Mg}_6\text{Si}_3\text{O}_{10}(\text{OH})_8$	System: Monoclinic	
Space Group: C2/m	Angles:	
$Z = n \times 2$	$a = 5.32 \text{ \AA}$	$\beta = 97^\circ$
	$b = 9.21 \text{ \AA}$	
	$c = n \times 14.2 \text{ \AA}$	

This is one of the simplest forms; other minerals show lower symmetry. Penninite is the most abundant true chlorite and the arrangement of atoms in the various layers is shown in Fig. III.20. If the chemical formula is represented as follows the structure may be more clearly appreciated:



brucite layer

talc layer

Other chlorites with a similar structure and differing only in the cations present include *clinochlore*, *corundophilite* and *prochlorite*, as well as some forms of *chamosite*.

All chlorites are of the trioctahedral series and are based on talc; there is apparently no chlorite with a structure related to pyrophyllite.

Mineralogists recognise a series of minerals from *antigorite* (see p. 140) with a single-layer trioctahedral kaolin-like structure, to *penninite*, the true chlorite. Antigorite has virtually no replacements of aluminium for silicon in tetrahedral co-ordination or for magnesium in octahedral positions. It cannot form a chlorite type structure because the hypothetical layers of talc and brucite would be electrically balanced and no ionic linking could result. Thermodynamically, the single-layer structure is probably more stable and therefore antigorite has this configuration.

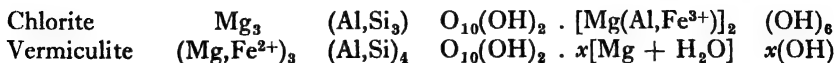
Vermiculites. Another distinct group of minerals which form large mica-like flakes are the *vermiculites*. When heated, these minerals *exfoliate* in an amazing fashion with an increase in volume up to 100-fold. As a result they are valuable in ceramics for thermal insulation. These minerals derive their name from their peculiar property after the Latin *vermiculare*—to breed worms.

Vermiculites are mainly hydrated magnesium silicates although considerable amounts of aluminium and iron may be present. Gruner¹ derived the average molecular composition of vermiculite as



although undoubtedly some of the magnesium is present in the form of an exchangeable base.

The structure may be compared with that of chlorite (Fig. III.20); the resemblance is shown in the structural formulæ:



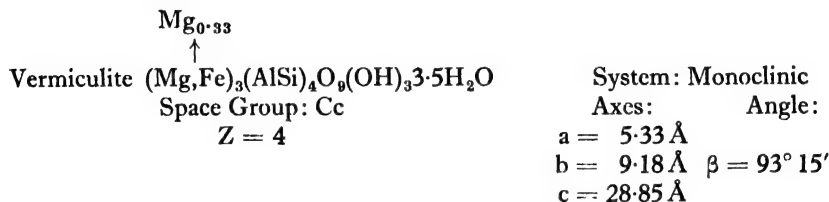
¹ Gruner, J. W., *Amer. Min.*, 24, 428, 1939.

In vermiculites, hydroxyl units or water molecules take the place of the brucite layers of chlorites and there is extensive hydration. The analogy between the two structures is complete when the exchangeable magnesium cations, which are fully hydrated,¹ are included between the electrically-unbalanced talc-like layers.

Normally, the basal spacing of vermiculite is 14.2 Å, but on heating to moderately high temperatures the lattice collapses to 9.26 Å. This takes place in two stages; an intermediate spacing of 11.8 Å results after dehydration at 110° C.

Walker² has suggested that those magnesium ions which are loosely held between the talc layers are hydrated normally; they lose part of their water at 110° C. and then finally collapse after the removal of all the water.

Hendricks and Jefferson³ give the structural constants as:



The *exfoliation* in vermiculite is apparently of two types, because it can be produced by two entirely different agencies.

(i) Rapid heating is one cause and presumably the explosive release of water molecules serves to push the layers of mineral apart. Slow calcination with gradual increase in temperature does not cause exfoliation and there is little expansion when the vermiculite particles are of small size.

(ii) Some vermiculites exfoliate on treatment with oxidising agents, such as hydrogen peroxide. Drosdoff and Miles⁴ suggest that extraneous material may be occluded between the plates which may decompose the peroxide and liberate oxygen. Such compounds include manganese dioxide, carbonaceous matter and various oxides.

Vermiculites are often confused with *hydrobiotites* which are really hydrous micas. Hydrobiotites always have associated alkalis and have a lower basal spacing.

MIXED-LAYER STRUCTURES

MANY layer-silicate minerals which occur in nature are composed of mixed layers of more than one type. Some are known which consist of units of mica, chlorite and vermiculite; in others hydrous mica and montmorillonite layers may be included. When mixed-layer structures occur, the interpretation of X-ray diffraction data is difficult, especially when the arrangement of layers is complex.

¹ Walker, G. F. and Milne, A. A., *Clay. Min. Bull.*, 1, 171, 1951.

² Walker, G. F., *Nature*, 163, 726, 1949.

³ Hendricks, S. B. and Jefferson, M. E., *Amer. Min.*, 23, 851, 1933.

⁴ Drosdoff, M. and Miles, E. F., *Soil Sci.*, 46, 391, 1938.

TRANSFORMATIONS BETWEEN THE LAYER-LATTICE MINERAL GROUPS

WITHIN the last few years, many workers have investigated the interconvertibility of the main mineral types. Physical chemists have attempted to reproduce in the laboratory, reactions which the mineralogists have recognised as taking place in nature. At present, the correlation of the two lines of investigation is far from complete and there is much conflicting evidence.

The conditions for the formation of the main clay mineral types are known with reasonable certainty and inferences can be made as to the changes which take place under varied conditions. As an example, the degradation of muscovite is thought to proceed through a hydrous mica or illite to a kaolin type of mineral, possibly always livesite, although the mechanism of the final stage in this transformation is not fully understood. It is easy to visualise the gradual decrease in alkali ion, but the process causing the conversion of a double-layer silicate to a single-layer one, and at the same time bringing about the elimination of charge deficiencies in the external silica network, must be more complex. Yet the weathering of mica appears to proceed so smoothly and easily in nature that one is tempted to speculate whether the mineral configurations are so rigid and inviolable as structural physicists believe.

Another well-defined series is recognised in the ferro-magnesian mineral group, which has biotite as its parent and progresses through chlorite or hydrobiotite again to a kaolin mineral with, perhaps, vermiculite and a montmorillonite type mineral as intermediates or new series. Such changes must indeed be speculative, even when based on sound mineralogical evidence, because laboratory experiments have not been able to confirm many of the major steps.

Noll¹ and Strese and Hofmann² have synthesised clay minerals under laboratory conditions and have shown that acidic conditions favour the formation of kaolin types or hydrous micas. Alkaline conditions, especially in the presence of magnesium or iron salts, produce montmorillonite types. Caillère and Henin³ have demonstrated that chlorite may be formed from montmorillonite in the presence of magnesium hydroxide. The interconvertibility of muscovite or biotite micas, montmorillonite and chlorite, under suitable conditions, is well established but no change to kaolin minerals has been fully proved. Within the kaolin group, the only change which has been confirmed is that between kaolinite and halloysite. In the region of mineral springs, rich in sulphate or chloride ions, kaolinite is known to form halloysite, but whether this is a true transformation or whether the clay mineral is dissolved and then reprecipitated has not been established.

Youell⁴ has summarised most of the changes which can be effected or are theoretically possible between the principal clay mineral types.

For a detailed consideration of the genesis, structure and composition of clay minerals, the reader may consult the publication on the subject by R. E. Grim.⁵

¹ Noll, W., *Neues. Jähr. Chem. der Erde.*, 10, 129, 1936.

² Strese, H. and Hofmann, U., *Zeit. anorg. All. Chemie.*, 247, 65, 1941.

³ Caillère, S. and Henin, S., *Min. Mag.*, 28, 612, 1949.

⁴ Youell, R. F., *Clay Minerals Bull.*, 1, 6, 1951.

⁵ Grim, R. E., *Clay Mineralogy* (McGraw-Hill Book Co., N.Y., 1953).

THE IDENTIFICATION OF CLAY MINERALS

ALTHOUGH there are many layer silicates, the various groups are well defined and can be recognised from various diagnostic data.

All the single-layer minerals have a basal spacing of about 7 Å whether they are of the dioctahedral series (like kaolinite) or the trioctahedral series (like antigorite or amesite).

Double-layer minerals may also be distinguished from each other by chemical and physical tests and the main differences may be summarised in Table III—XI.

ACTION OF HEAT ON LAYER SILICATES

THE effect of heat on the atomic arrangement of layer silicates shows a remarkable similarity between all minerals, and a simple pattern emerges.

Heating at a comparatively low temperature (up to 700° C.) will usually drive off any molecules of combined water without distorting the structure; indeed kaolinite, which has been dehydrated at temperatures up to 750° C., can be rehydrated almost quantitatively by treatment in an autoclave.

At higher temperatures most of the octahedrally co-ordinated cations such as aluminium, iron, and magnesium retain their special positions, but the tetrahedra of silica appear to be capable of migration. Crystallisation phenomena may occur, such as the formation of γ -alumina, but invariably the first combination product is a silicate with an island group structure. Thus aluminium-bearing layer silicates, such as kaolinite and montmorillonite, give mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$); magnesium minerals form forsterite (Mg_2SiO_4); whilst olivine is produced on heating an iron-magnesium mineral.

Prolonged heating may also result in the formation of other silicates with more complex structures.

All layer silicates in this section are based on the hexagonal ring structure of silica. This is by far the most common configuration, but minerals are known where the silica layer is of rings with less than six units. *Apophyllite* is an instance where four silica groups are linked into a ring formation extending in two dimensions.

5. FRAMEWORK STRUCTURES

TO complete the possible silicate structures, those must be included where all four of the oxygens tetrahedrally linked to a particular silicon are also shared with other silicon atoms. In these, every oxygen is linked to two silicon atoms and receives one valency share from each. By this means, electrical balance is maintained throughout the resulting three-dimensional framework.

Theoretically, all structures of this type must have the chemical composition SiO_2 , but substitution can occur and many important minerals are of this group.

THE SILICA MINERALS

EVEN among the minerals which are composed entirely of silica there is complexity of structure. Silica occurs in many forms in nature; three distinct *crystalline*

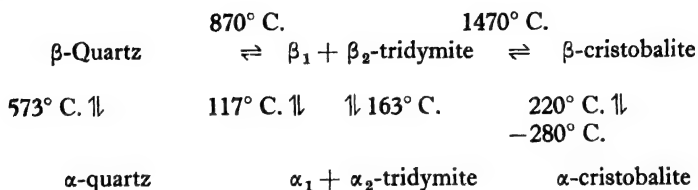
TABLE III—XI. DISTINGUISHING FEATURES OF DOUBLE-LAYER SILICATES

	<i>Main Minerals</i>	<i>Composition</i>	<i>Basal Spacing</i>	<i>Other Distinguishing Features</i>
Electrically Balanced Layers	Pyrophyllite Talc	$\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	9.25 Å 9.40 Å	
Electrically Unbalanced Layers				
1. Montmorillonite-type Minerals	Montmorillonite	$\text{Na}_{0.33}$ \uparrow $(\text{Al}_{1.67}\text{Mg}_{0.33})\text{Si}_4\text{O}_{10}(\text{OH})_2$ $\text{Na}_{0.33}$ \uparrow $(\text{Al}_{1.22}\text{Al}_{1.78}\text{Si}_3)\text{O}_{10}(\text{OH})_2$ As above but with Fe^{3+} ions $\text{Na}_{0.33}$ \uparrow $(\text{Mg}_{2.67}\text{Li}_{0.33})\text{Si}_4\text{O}_{10}(\text{OH})_2$ $\text{Na}_{0.33}$ \uparrow $\text{Mg}_3(\text{Al}_{0.33}\text{Si}_{3.67})\text{O}_{10}(\text{OH})_2$	<i>circa</i> 14 Å	The 14 Å spacing may be expanded by treatment with water or glycerol
2. Micaceous Minerals	Muscovite Lepidolite Biotite	$\text{KAl}_2(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$ $\text{K}(\text{Al}, \text{Li})_2(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$ $\text{K}(\text{Mg}, \text{Fe})_2(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$	9.9–10.1 Å	High alkali content
3. Hydrous Micaceous Minerals		Variable	9.9–10.1 Å	Lower alkali, higher water content than true mica
4. Chlorites	Penninite	$\text{Mg}_3(\text{Al}, \text{Fe}^{3+})(\text{Al}, \text{Si})_4\text{O}_{10}(\text{OH})_8$	14 Å	
5. Vermiculite		$(\text{Mg}, \text{Fe}^{3+})_3(\text{Al}, \text{Si})_5\text{O}_{10}(\text{OH})_2 \cdot 3.5\text{H}_2\text{O}$	14 Å	Heat treatment reduces basal spacing to 11.8 Å

varieties are recognised, *quartz*, *tridymite* and *cristobalite*. All the three polymorphic forms are capable of existing in more than one modification, with different crystal structures.

The interrelationship between these minerals is of great importance in the manufacture and use of silica and siliceous refractory materials.

The temperature stability ranges of the various modifications of silica may be summarised as:



Each form has a limited temperature stability range.

There are two distinct types of transformations in silica minerals:

(a) The *conversions*, where quartz changes to tridymite and then to cristobalite. These changes involve a fundamental structural rearrangement; β-quartz is hexagonal whilst β-tridymite is trigonal and β-cristobalite is cubic. Although these transformations are reversible, the rate of change is normally exceedingly slow. Pure quartz crystal can be raised to the melting point at 1680° C. and eventually melted completely without any appreciable conversion into cristobalite or tridymite taking place. Similarly, cristobalite, which is theoretically metastable at normal temperatures, would revert to quartz only in a length of time equivalent to a geological age. Some of the changes may, however, be accelerated by catalytic agents.

(b) The *inversions*, which are the transitions between the α and β varieties of the minerals, involve only slight structural rearrangements and the changes are instantaneously reversible.

Both conversions and inversions are accompanied by a change in the density of the silica.

The β-modifications of all these minerals are stable at the higher temperatures and these have the most symmetrical structures. As the structure of all the silica minerals is based on linked silica tetrahedra (SiO₄)⁴⁻, any variations in structure must be the result of the way in which these tetrahedra are combined. If two tetrahedra are linked together through one common oxygen there are three possibilities as shown in Fig. III.22. In the first two diagrams (A) and (B) the Si—O—Si angle is 180° in both cases, but in (A) the top three oxygen atoms are the mirror image of the lower ones, whilst in (B) the upper layer has been rotated through 180° with respect to the lower one. The third alternative (C) is when the units are not arranged linearly and the top unit is inclined at an angle to the lower one.

These three arrangements illustrate the essential differences between the β-modifications of tridymite, cristobalite and quartz. The (A) type of linking, or the *cis*-form as it is called, is the structural scheme of tridymite; the *trans*-form (B) is that of cristobalite; whilst quartz is unit (C) extended in space.

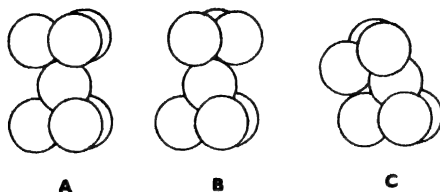


FIG. III.22. THE IDEAL DISPOSITIONS OF ADJACENT SILICA TETRAHEDRA IN THE SILICA MINERALS
(A) Tridymite; (B) cristobalite; and (C) quartz.

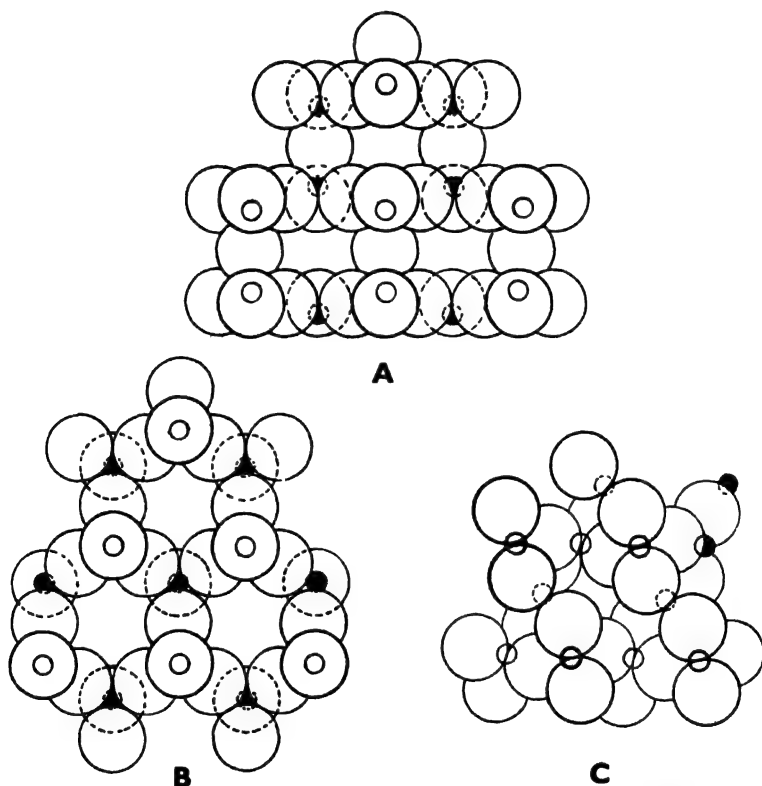


FIG. III.23. THE IDEALISED STRUCTURES OF THE SILICA MINERALS
(A) Tridymite; (B) cristobalite; and (C) quartz.

The complete structures are shown in Fig. III.23 A, B and C.

It is difficult to illustrate the structure of quartz in a way which brings out all the details. The relative positions of adjacent tetrahedral units produce a spiral formation throughout the crystal. The direction of twist of the spirals determines whether the crystal is left- or right-handed.

The crystal structures of both tridymite and cristobalite are more open than that of quartz; this accounts for the much lower density of these forms of silica.

The conversions of the silica minerals involve a complex rearrangement within the crystal. Bond angles have to change and considerable rotational and translational displacements are necessary for the change from one form to another. It is not surprising, therefore, that such changes are sluggish and take place only with difficulty.

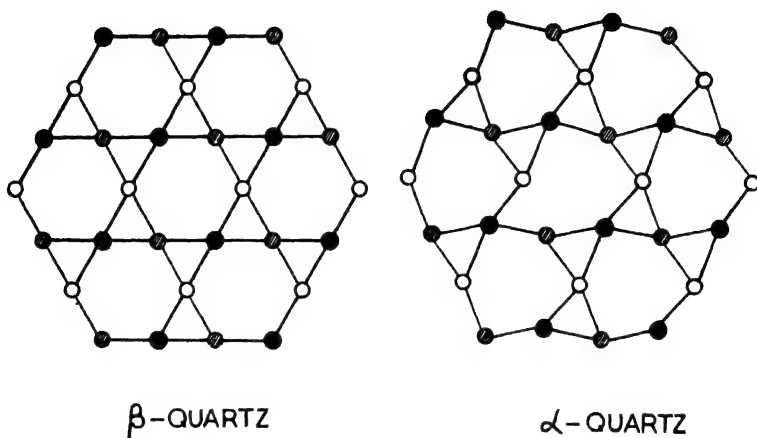


FIG. III.24. DIAGRAMMATICAL REPRESENTATION OF THE α - TO β -QUARTZ INVERSION
The small circles represent silicon atoms in three planes (cf. Fig. III.23).

The inversional change is much simpler. The β -form of the minerals, which is stable at high temperatures, is symmetrical. When the inversion occurs the crystal is deformed and assumes a lower symmetry. Cristobalite, tridymite and sometimes quartz are formed at high temperatures, therefore the β -modification is produced, but as the crystals cool, contraction occurs and eventually distortion results. Bond angles are altered and the structure becomes more dense. The structural change from α - to β -quartz has been deduced by R. E. Gibbs¹ and the atomic configuration of the two forms is shown in Fig. III.24. It will be appreciated that although the α -modification is a distorted form of β -quartz, the same general atomic arrangement is maintained and there is no bond breaking and no ionic migration.

The inversion of tridymite has not been deduced with certainty and is complicated because it appears to take place in two stages. Grimshaw, Westerman and Roberts² have demonstrated that at least two forms of tridymite exist, an α_1 variety which inverts to β_1 at 117° C. and α_2 inverting to β_2 at 163° C. It has not yet been possible to isolate these forms in a pure state nor to investigate the inversional change in detail. The change from $\alpha \rightarrow \beta$ cristobalite has been investigated by Nieuwenkamp.³ He considers that in the β - or high-temperature variety the oxygen atoms

¹ Gibbs, R. E., *Proc. Roy. Soc.*, **A110**, 443, 1926.

² Grimshaw, R. W., Westerman, A. and Roberts, A. L., *Trans. Brit. Ceram. Soc.*, **47**, 269, 1948.

³ Nieuwenkamp, W., *Zeit. Krist.*, **96**, 454, 1937.

are rotating in small circular orbits about a line joining silicon atoms. After inversion to the α -form the oxygen ions are 'frozen' in random positions about these circular orbits, but always maintaining a Si—O—Si bond angle of about 150° . In the high-temperature form of cristobalite, the distance from the centre of one silicon atom, through an oxygen to the centre of the next silicon atom is 3.08 \AA , but in the α -form, the separation distance is 3.067 \AA .

The Mechanism of the Transformations of Silica Minerals. As explained on p. 160, when silicates are heated, the tetrahedral units of silica $(\text{SiO}_4)^{4-}$ appear to dissociate and to be capable of migration. On cooling, they reform around other ions or groups in such a manner as to form the most stable configuration.

When quartz is heated, it is converted slowly into tridymite or cristobalite but the change can be accelerated by the addition of other cations, some of which catalyse the formation of cristobalite (examples are Ca^{2+} , Mg^{2+} , Fe^{2+} and Ba^{2+} ions), whilst others (mainly alkali ions) promote the formation of tridymite. Some other cations (principally Al^{3+} and Ti^{4+}) do not appear to assist the conversion of quartz, indeed, alumina tends to retard it.

It is probable that when such cations are present, the silica tetrahedra which are dissociated at high temperatures, nucleate around them. The larger the sphere of influence of the cation, the more open will be the silica configuration around it and hence the less dense will be the resulting silica form. Tridymite has the most open lattice of the silica minerals with spaces as large as 2.5 \AA , cristobalite has also an open structure but with voids of smaller size, and quartz is much more dense. Cations with the largest range of influence may nucleate tridymite; but as the size is reduced the formation of cristobalite would be favoured and, finally, very small spheres will produce the closest packing of the quartz lattice.

The different effects of various cations does not depend entirely on their ionic radii, for although a large ion, like potassium (K^+) with a radius of 1.33 \AA , facilitates the formation of tridymite, lithium (Li^+) with a radius of 0.78 \AA behaves similarly, but barium (Ba^{2+}) (radius 1.43 \AA) catalyses the formation of cristobalite. Dietzel¹ considers that the activity of cations in glasses is related to their field-strength at the separation distance of surrounding anions, i.e. the charge per unit surface area of a sphere equivalent in size to the radius of cation and anion. If cations are regarded as spheres, the field-strength will be proportional to Z/a^2 where Z is the charge on the cation and a is the radius of cation (r_c) plus that of the anion (r_a).

Table III.XII shows that the value of Z/a^2 is related to the ability of the various cations to catalyse the formation of tridymite and cristobalite from quartz. Aluminium and similar cations which do not accelerate the rate of conversion to any great extent may be classified as *quartz-formers*.

Another theory advanced to explain the catalytic conversion of silica is that the oxides form silicate compounds which 'seed' the formation of one of the various forms. This is really only another way of expressing the field-strength, for the cations present govern the configuration of the surrounding silica tetrahedra.

Considerable support for these theories is found in a study of compounds which are isostructural with the silica minerals.

¹ Dietzel, A., *Zeit. Elektrochem.*, 48, 1, 9, 1942.

TABLE III—XII. EFFECTS OF VARIOUS CATIONS IN CATALYSING SILICA

Cation	Ionic radius	$a = (r_c + r_a)$	$\frac{Z}{a^2}$	Effects
K ⁺	1.33 Å	2.65 Å	0.12	} Tridymite-forming catalysts
Na ⁺	0.98	2.30	0.19	
Li ⁺	0.78	2.10	0.22	
Ba ²⁺	1.43	2.75	0.24	} Cristobalite-forming catalysts
Ca ²⁺	1.06	2.38	0.33	
Fe ²⁺	0.83	2.15	0.43	
Mg ²⁺	0.78	2.10	0.44	} Quartz-forming catalysts
Be ²⁺	0.34	1.66	0.86	
Al ³⁺	0.57	1.89	0.84	
Ti ⁴⁺	0.69	2.00	1.00	

MINERALS ISOSTRUCTURAL WITH SILICA MINERALS

HUMMEL,¹ in 1949, described the structural relationships of *aluminium phosphate*, AlPO_4 , which exists in three forms resembling quartz, cristobalite and tridymite.

Of more importance to ceramists are the minerals *nephelite*, NaAlSiO_4 , and *disodium calcium silicate*, $\text{Na}_2\text{CaSiO}_4$, which have been described by Barth and Posnjak² and Buerger.³

Nephelite is an important mineral in glaze manufacture and is used extensively in the ceramic industry as a substitute for feldspar. It has a crystal form which is similar to tridymite, with the difference that every alternate silicon atom (Si^{4+}) is replaced by aluminium (Al^{3+}), thereby causing a unit-charge deficiency which is balanced by the introduction of a sodium ion (Na^+).

The replacement is $\text{Na}^+ \text{Al}^{3+} \rightleftharpoons \text{Si}^{4+}$.

Sodium ions are contained in the vacant sites within the lattice and are held firmly by ionic bonding. The structure does not undergo any change resembling inversion but, at 1248° C., nephelite changes to carnegieite which converts back very slowly to the original form on cooling. *Carnegieite* is cubic at high temperatures and is identical with β -cristobalite except for the isomorphous substitutions. Furthermore, on cooling, its high-temperature form inverts to a distorted form at 690° C. Sodium ions occupy only part of the vacant sites so inversion can take place, through a change in bond angles.

Disodium calcium silicate, $\text{Na}_2\text{CaSiO}_4$, is cubic at all temperatures and, like carnegieite, has the same structure as cristobalite. Calcium ions (Ca^{2+}) replace silicon, so there are two unit-charge deficiencies for each replacement; these are balanced by two sodium ions. Sodium ions fill all vacant lattice-sites and so the structure is close-packed and no inversion can take place. Further studies of these and similar isostructural minerals may throw more light on the conversions of silica.

¹ Hummel, F. A., *J. Amer. Ceram. Soc.*, 32, 320, 1949.

² Barth, T. F. W. and Posnjak, E., *Zeit. Krist.*, 81, 376, 1932

³ Buerger, M. J., *Amer. Min.*, 33, 751, 1948.

They do establish that alkali ions can enter the lattice of these minerals and influence the crystal form.

According to Buerger¹ (1954) there are many minerals which have the same structure as the silica minerals, but with isomorphous substitutions. The replacement of a silicon ion by aluminium or a similar-sized cation involves no special disarrangement, but the resulting positive charge deficiency has to be made up by the inclusion of other cations in the voids in the lattice. The size of the balancing cation influences the structure of the so-called 'stuffed' derivatives.

If the structure is that of quartz, then the included cations must be small, e.g. Li, Be, or B, to fit the voids; hence, *eucriptite*, LiAlSiO_4 and $\text{LiAlSi}_2\text{O}_6$ are of this type.

When the voids in the structure are larger, as in the tridymite or cristobalite lattice, then larger cations can be incorporated. As would be expected, very large cations can fit only into the tridymite structure and so most potassium derivatives are of this form, e.g. KAlSiO_4 , $\text{K}_2\text{MgSi}_3\text{O}_8$ and $\text{K}_2\text{FeSi}_3\text{O}_8$. The inclusion of sodium cations is most usual in cristobalite-type structures, some examples of which have already been quoted.

Isomorphous replacement in silica minerals is probably the rule rather than the exception. Keith and Tuttle² have reported that the cause of anomalous inversion temperatures in quartz, when prepared under different conditions, might be due to solid solution or replacements. Quartz containing incorporated lithium and aluminium gave a low inversional change, but if germanium (Ge^{4+}) ions were incorporated, the temperature of the change was much increased (see also p. 690).

OTHER FORMS OF SILICA

IN addition to the different crystalline modifications already mentioned, silica exists in nature in other forms; these include *flint*, *chert*, *chalcedony*, *agate*, *opal*, *geyserite* and *silica gel*.

Many of these varieties are amorphous or crypto-crystalline in character, but some have a pseudo- or distorted-type of quartz lattice.

Recent work on the grinding of quartz has shown that a distorted layer is formed on the surface and the crystalline form of quartz is destroyed.³ Most samples of natural silica are sedimentary in origin and, in many instances, mechanical erosion during transportation has distorted the minute crystallites.

Opal is a variety of hydrated silica with a composition $\text{SiO}_2 \cdot n\text{H}_2\text{O}$. It is the main constituent of kieselguhr or diatomaceous earth.

FELSPARS

THE most common constituents of igneous rock formations are the *felspars*. These important minerals are used extensively in the manufacture of porcelains, stoneware,

¹ Buerger, M. J., *Amer. Min.*, 39, 600, 1954.

² Keith, M. L. and Tuttle, O. F., *Amer. J. Sci.*, 203, 1952.

³ Dempster, P. B. and Ritchie, P. D., *Nature* (London), 169, 539, 1952.

Nagelschmidt, G., Gordon, R. L. and Griffin, A. G., *Nature* (London), 169, 539, 1952.

TABLE III—XIII. THE FELSPAR GROUP
(After Taylor)

Crystal habit	Mineral	Composition	Space group	Crystallographic dimensions					
				a	b	c	α	β	γ
Monoclinic	Orthoclase	KAlSi_3O_8	C2/m	8.4 Å	12.9 Å	7.1 Å	—	116°	—
	Hyalophane	$\left\{ \begin{array}{l} \text{KAlSi}_3\text{O}_8 \\ \text{BaAl}_2\text{Si}_2\text{O}_8 \\ \text{BaAl}_2\text{Si}_2\text{O}_8 \end{array} \right.$	"	8.63	13.10	7.29	—	116°	—
	Celsian	$\text{BaAl}_2\text{Si}_2\text{O}_8$	"	8.44	13.00	7.21	90° 07'	115° 50'	89° 55'
Triclinic	Microcline	KAlSi_3O_8	"						
	Albite (Ab)	$\text{NaAlSi}_3\text{O}_8$	C	8.14	12.86	7.17	94°	116° 30'	89°
	Oligoclase	Ab_6An to Ab_8An	"	8.14	12.86	7.17	93° 23'	116° 28'	89° 59'
	Andesine	Ab_3An to AbAn	"						
	Labradorite	AbAn to AbAn_2	"						
	Bytownite	AbAn_2 to AbAn_4	"						
	Anorthite (An)	$\text{CaAl}_2\text{Si}_2\text{O}_8$	"	8.21	12.95	14.16	93° 13'	115° 56'	91° 12'

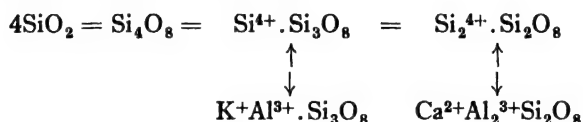
earthenware and many kinds of engobes and glazes and are common constituents of alumino-silicate slags.

There are three clearly-defined groups: (i) based on *orthoclase*, KAlSi_3O_8 , (ii) termed the *plagioclase* group, which are solid solutions of *albite*, $\text{NaAlSi}_3\text{O}_8$, and *anorthite*, $\text{CaAl}_2\text{Si}_2\text{O}_8$, and (iii) *celsian*, $\text{BaAl}_2\text{Si}_2\text{O}_8$, which is not of common occurrence. There are also the *felspathoids*, such as *leucite*, KAlSi_2O_6 , and *nephelite*, NaAlSiO_4 .

Orthoclase and celsian are monoclinic crystals which are soluble in each other in virtually all proportions, yet they have a limited solubility in triclinic plagioclase. The important feldspars are classified in Table III.XIII which also gives their crystallographic details.

Orthoclase and albite undergo inversion at high temperature, changing to *sanidine* and *barbierite* respectively.

The structure of all feldspars is based on a framework of SiO_2 , but one which is more open than that of the silica minerals. There is replacement of silicon by aluminium ions however, which results in charge-deficiencies, balanced by cations of K^+ , Na^+ , Ba^{2+} or Ca^{2+} entering the lattice thus:



Albite, $\text{NaAlSi}_3\text{O}_8$, is isomorphous with *anorthite*, $\text{CaAl}_2\text{Si}_2\text{O}_8$, therefore Na^+ Si^{4+} must be equivalent to and capable of being substituted by Ca^{2+} Al^{3+} , and so albite and anorthite may be regarded as the end members of a complete series of solid solutions which are termed the plagioclase feldspars.

The framework structure of the feldspars is based on condensed rings of four tetrahedra as shown in Fig. III.25. A type of chain structure results which is linked to similar formations on all sides, thus forming a three-dimensional framework. The resulting structure contains voids large enough to hold extra cations which electrically balance the lattice.

In orthoclase, one silicon atom in every four is replaced by aluminium, but it is not possible to show by X-ray studies whether such substitution is regular or random.

Feldspars change to kaolinite under suitable weathering conditions yet the structural mechanism remains a complete mystery. The two configurations are very different, and if present concepts are correct, then extensive rearrangement would be necessary.

ZEOLITES

THE zeolites are also based on framework structures of $(\text{Si},\text{Al})\text{O}_2$ units, but the lattice is more open than that of the feldspars, and cavities and wide channels are present.

The framework has a net charge-deficiency which is electrically balanced by large-sized cations contained in the voids in the lattice. Unlike those in the feldspar structure, these cations are not held firmly, but can move freely within the more open cavities and channels. Consequently they can be readily exchanged and, in

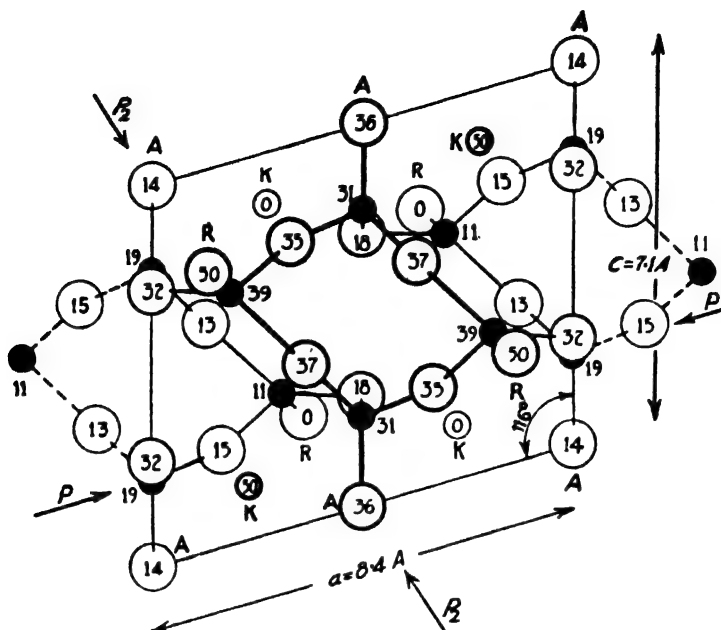


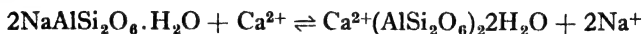
FIG. III.25. THE IDEALISED STRUCTURE OF ORTHOCLASE FELSPAR
(after Taylor)

The small numbers refer to the heights of atoms above a zero plane. The chain formation along the a -direction is clearly shown.

addition, large quantities of water may be contained which can be driven off by heat without destroying the structure. In addition to absorptions of this type, other substances such as ammonia, carbon dioxide, alcohol, iodine and mercury may penetrate along the channels. Zeolites are of three types with cubic, fibrous or lamellar form.

Analcite, $\text{NaAlSi}_3\text{O}_8 \cdot \text{H}_2\text{O}$, is an example of a cubic zeolite; *natrolite*, $\text{Na}_2(\text{Al}_2\text{Si}_3\text{O}_{10})2\text{H}_2\text{O}$, and *edingtonite*, $\text{Ba}(\text{Al}_2\text{Si}_3\text{O}_{10})4\text{H}_2\text{O}$, are fibrous and *heulandite*, $\text{Ca}(\text{Al}_2\text{Si}_7\text{O}_{18})6\text{H}_2\text{O}$, has a sheet-structure.

The zeolites are commonly employed as water softeners as a result of their capacity for cationic exchange. A sodium zeolite will readily adsorb calcium ions from solution thus:



The original zeolite can be regenerated by treatment with a solution of sodium chloride.

THE STRUCTURE OF GLASS

SOME substances, which are of common use as ceramic materials, do not crystallise readily after being melted at high temperature and then being allowed to cool. The resulting product behaves as a super-cooled liquid, in that there is a gradual alteration in properties during the change from the liquid to the solid state and no sharp

temperature of demarcation between the two phases is shown. Substances of this nature are termed *glasses* and they are non-crystalline, isotropic and usually transparent. Glasses do not give a regular X-ray pattern, therefore the crystal structure cannot be regular as is the case in a truly crystalline material; the arrangement of atoms is random and there is no unit cell of structure which repeats at regular intervals in space.

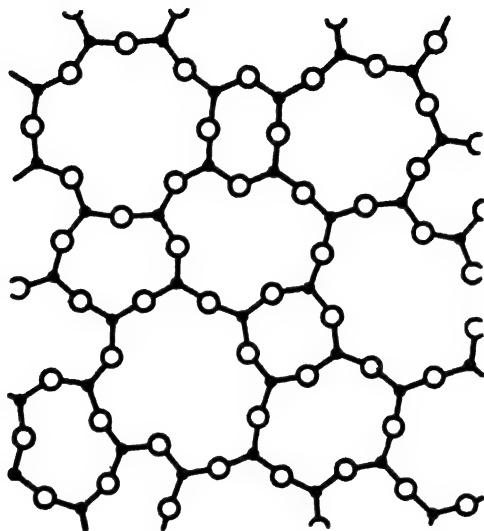


FIG. III.26. THE STRUCTURE OF SILICA GLASS
(after Zachariasen)

In all the crystal structures described in the preceding pages, certain laws must be obeyed in the building-up of units, and such units must 'repeat' at frequent intervals throughout a three-dimensional space. In accordance with modern theories of the structure of glass, the same laws apply to the unit construction, but there is no regular order or arrangement in the building-up of such units into the glass structure.

This may be more clearly appreciated by considering *silica*, which is the most commonly-employed glass-former.

It is well known that, at high temperatures, ordered silicate lattices dissociate, mainly because the individual silica tetrahedra $(\text{SiO}_4)^{4-}$ become detached and are free to migrate. On cooling, the units come together, bonds are reformed and usually a symmetrical arrangement is produced before the material becomes completely solid. If the temperature is lowered rapidly, there is a tendency for the liquid to become too viscous before the units can form into an ordered lattice. The resulting solid behaves as a super-cooled liquid and is termed *glass*.

The difference between a symmetrical crystal formation and a randomly arranged lattice of glass is represented diagrammatically in Fig. III.26. The true picture is, of course, an extension of such structures in three dimensions. An

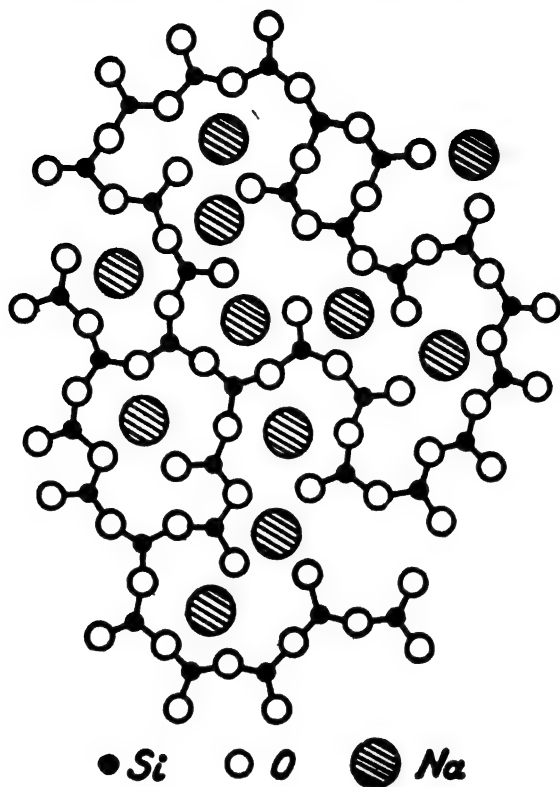


FIG. III.27. THE STRUCTURE OF ALKALI-SILICA GLASS

important point is that in silica glass, discrete $(\text{SiO}_4)^{4-}$ units are present with tetrahedrally co-ordinated groups. These are linked to other similar units through common oxygen atoms so that the structure is electrically balanced. The Si—O distance remains the same as in true crystalline structures, but the Si—O—Si angle is variable and capable of distortion through wide angles.

Zachariasen¹ first suggested this structure for glass in 1932 and his ideas have been subsequently confirmed by Warren² and co-workers following careful analytical X-ray studies.

When other cations are added to silica, the glass structure is more complex, but the same general laws are obeyed. A glass made of soda and silica serves as a useful example. The sodium cations occupy holes in the glass structure and electrical balance is maintained by an oxygen atom being linked to only one silicon as in Fig. III.27. As more sodium ions are incorporated, the tendency to form glass is diminished and definite compounds with ordered lattices readily crystallise on cooling.

¹ Zachariasen, W., *J. Amer. Chem. Soc.*, **54**, 3941, 1932.

² Warren, B. E., *J. Applied Physics*, **13**, 602, 1942.

As a result of such observations, Zachariasen was able to postulate that the conditions required for a chemical compound to be capable of forming a glass are:

(a) That the anions in the glass structure should each be linked to not more than two cations. Where this is not the case, too rigid bonding can occur and there can be no distortion of the linkages.

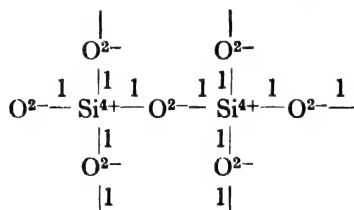
(b) That the number of anions about each cation (i.e. the co-ordination number of the cation) must be small.

(c) That the anionic polyhedra (equilateral triangles, tetrahedra, octahedra, etc.) must share corners and not edges or faces with other like polyhedra, otherwise the bonding will be too rigid.

(d) That at least three corners of each anionic polyhedron must be linked to other similar units if a three-dimensional network is to be formed.

On the basis of these four stipulations, it is easy to deduce those compounds which will form glasses.

Zachariasen's first postulate (a) excludes most oxides because very few cations form oxides where each oxygen atom is electrically balanced by being linked to only two cations. Silica is an exception, as four anions surround a quadrivalent silicon ion (Si^{4+}) and receive one valency share each. Therefore, if each oxygen (O^{2-}) is linked to two silicon atoms it is electrically balanced, and a glass can form.



Aluminium (Al^{3+}) may form six-fold (octahedral) or four-fold (tetrahedral) co-ordinated groups with oxygen. In the former case, each oxygen receives only a half-valency share from an aluminium cation and would require to be linked to three others and could not form glass. In the second case (tetrahedral grouping), each oxygen around an aluminium ion receives three-quarters of a valency share. To achieve electrical balance, each oxygen must be linked to an average of 2.66 aluminium ions and under these conditions glass can again, theoretically, not be formed.

The glass-forming capacity of an oxide is thus dependent on the size and charge of the cation. The former determines the co-ordination number and the latter the valency-contribution to each oxygen atom. It may be concluded that:

A *monovalent oxide* (M_2O) cannot form a glass.

A *divalent oxide* (MO) cannot form a glass because the cation would have to be linked to only two oxygens, and a three-dimensional network could not be formed.

A *trivalent oxide* (M_2O_3) can form a glass if the cation is in threefold co-ordination. By reference to Table II.XIII (p. 84) it will be seen that B_2O_3 is the only trivalent oxide which can be a glass-former, although As_2O_3 and Sb_2O_3 may be so in certain circumstances.

A *quadrivalent oxide* (MO_2) is a glass-former if the cation is in three- or four-fold co-ordination, or has a radius less than 0.5 Å. Silica (SiO_2) and germania (GeO_2) fulfil these requirements.

A *pentavalent oxide* (M_2O_5) again cannot have more than tetrahedral co-ordination if it is to be a glass-former, and phosphorus pentoxide (P_2O_5) and arsenic oxide (As_2O_5) are the only possibilities, although Sb_2O_5 , Cb_2O_5 and Ta_2O_5 are border-line cases.

Oxides of higher valency cations do not form glasses.

In general the only oxides which can form glasses are those with a co-ordination of three or four and with one of the following formulæ: M_2O_3 , MO_2 or M_2O_5 . There are five such oxides, *boron oxide* (B_2O_3), *silica* (SiO_2), *germania* (GeO_2), *phosphorus pentoxide* (P_2O_5), and *arsenic oxide* (As_2O_5). *Arsenious oxide* (As_2O_3) and *antimony oxide* (Sb_2O_3) will form glass, but with more difficulty than the others, and P_2O_3 , V_2O_5 , Sb_2O_5 , Cb_2O_5 and Ta_2O_5 are claimed to be glass-formers in exceptional circumstances. Arsenic and antimony are interesting because they can form glasses even when in six-fold co-ordination with oxygen. Apparently three of their oxygens are nearer the cation than the others and the unit behaves almost as though there were three-fold co-ordination.

Some other compounds may form glass, e.g. *beryllium fluoride*. Fluorine atoms are similar in size to those of oxygen, but are monovalent. Although in beryllium fluoride, the beryllium ions (Be^{2+}) are surrounded by four fluorine atoms, they give a half-valency share to each, and therefore each fluorine atom need be linked to only two cations and the Zachariasen laws are obeyed.

Some other cations can take part in the network structure of the true glass-formers, e.g. aluminium can replace silicon ions over a wide range of composition and form aluminosilicate glasses. Titanium, zirconium and tantalum can behave in similar fashion.

Other ions which play a large part in the structure of glass, yet can take no part in the network system, include the alkali metal cations Li^+ , Na^+ , K^+ , Rb^+ , and Cs^+ and the alkaline earth cations Ca^{2+} , Sr^{2+} , Ba^{2+} . Beryllium (Be^{2+}) and magnesium (Mg^{2+}) are of this group, though they may also, to some extent, enter the network system, as does aluminium. These large cations occupy holes in the network and serve to balance valency deficiencies which may arise through isomorphous substitutions in the network, or from unsatisfied oxygen atoms. These cations are important, for they act as nuclei around which the network forms and so they determine the size of the holes in the lattice.

One anomalous feature of glass structures is that lead (Pb) can take part in the network structure of silica or boron oxide. Stanworth¹ has suggested that the reason is attributable to the electron configuration in the outermost electron orbits of lead atoms. Table II.III (p. 69) shows that there are $(18 + 2)$ electrons in the penultimate orbit of the valency electrons, and such a unit is capable of easy deformation and forms covalent bonding. Thallium and bismuth behave similarly and impart refractivity to the resulting glass. Zinc and cadmium have an outer completed orbital of 18 and can also form part of the glass network.

¹ Stanworth, J. E., *J. Soc. Glass Tech.*, 32, 154, 1948.

Stanworth has also pointed out that the linkages in all glass structures are mainly covalent and he suggests that this covalency is essential before a lattice can be formed.

The cations which take part in oxide glass structures can be divided into three groups:

- (i) Those which form the network structures;
- (ii) Those which cannot form networks by themselves, but may replace other true glass-forming cations in the lattice;
- (iii) Those which occupy vacant holes in the network.

These are summarised in Table III.XIV.

TABLE III—XIV. ROLE OF CATIONS IN GLASS STRUCTURES

<i>Glass lattice-forming cations</i>		<i>Cations capable of replacing lattice- forming cations in network</i>		<i>Other cations capable of entering network</i>		<i>Cations which occupy holes in lattice</i>	
<i>Cation</i>	<i>Valency</i>	<i>Cation</i>	<i>Valency</i>	<i>Cation</i>	<i>Valency</i>	<i>Cation</i>	<i>Valency</i>
P	5	Ta	5	Bi	3	Ca	2
As	5	Ti	4	Pb	2	Sr	2
Si	4	Zr	4	Tl	1	Ba	2
Ge	4	Al	3			Li	1
B	3	(Be)	2	Cd	2	Na	1
(As)	3	(Mg)	2	Zn	2	K	1
(Sb)	3					Rb	1
V	5					Cs	1
Sb	5					(Be)	2
Cb	5					(Mg)	2
Ta	5						
P	3						

Glazes, Vitreous Enamels, Fritts and some *Fluxes* resemble glasses in their general structure and properties. They are described in Chapter VI.

CHAPTER IV

THE CRYSTAL STRUCTURE OF NON-SILICEOUS CERAMIC MATERIALS

FOR many years, the term *ceramic* was used almost exclusively for clays and clay products, but as the demands increased for furnaces and crucibles which could withstand higher temperatures and more prolonged heating than those made of *fireclay*, more attention was paid to other materials—particularly those of a high refractoriness which could be shaped and fired like clays.

Silica was the first of these non-argillaceous substances to be used, then *plumbago* or *graphite* was mixed with fireclay to increase the heat-resisting property. Various oxides of a highly refractory nature, such as *magnesia*, *lime*, *zirconia*, *titania*, *beryllia*, etc., were introduced, as also were *carbides* of such elements as silicon and boron. In recent years, *nitrides*, *borides* and other unusual compounds of rare elements have been manufactured for highly specialised application where extremely high temperatures are encountered, so that today large quantities of non-clayey materials are used industrially and must be included under the term *ceramic materials*.

The chief property of most of these non-siliceous materials is their great resistance to heat (refractoriness) which enables them to be used at very high temperatures. Other factors may also be involved, such as resistance to molten metals and slags or to their capability of withstanding high thermal or mechanical stresses. New ceramic bodies have been developed where other properties are the main consideration; these include materials of low thermal conductivity or resistivity, those with special electrical properties and those with unusually low expansion characteristics. In many cases, the valuable properties of the materials can be explained from their crystal structures and such studies have often led to improvements in performance.

Various non-siliceous materials are of great importance as opacifying and colouring agents and for the decoration of porcelain, chinaware and some domestic earthenware. Others are used as fluxes in bodies, engobes and glazes.

There are other non-siliceous minerals which, although of little value as ceramic materials, are present as impurities in some otherwise useful materials. These are among the most serious causes of defects in bricks, tiles, pottery, refractory materials and other ceramic articles, and as they are difficult if not impossible to eliminate, only a thorough knowledge of their nature and structure can provide means for reducing their deleterious properties to a minimum.

It is obviously impossible and undesirable to consider in detail all the minerals which are present in unfired and fired ceramic material, as it is a safe presumption that these would include most of the minerals so far discovered. Only those which occur most commonly in important ceramic materials will be considered.

ELEMENTS

THE number of *elements* which are to be found as such in ceramic materials is limited. The only one of importance is carbon, although gold, silver, platinum and some others are used to a limited extent for decoration and as colourisers for glazes.

CARBON

CARBON occurs in the free state in two varieties.

(a) **Amorphous.** As a soft, black mass or powder in *lampblack*, *soot*, *retort-scurf*, etc. Very little is known of its fundamental structure.

(b) **Crystalline as diamond and graphite.**

The *chief forms* of carbon as a ceramic material are:

(i) As a *refractory material*, in a graphitic form and used under reducing conditions.

(ii) As an *abrasive*, as diamond which is unequalled in hardness by any other substance.

(iii) As a constituent of the *carbonaceous matter* of many clays and sedimentary deposits.

Diamonds have long been known as crystals of exceptional beauty and hardness and were one of the first minerals to be analysed structurally by X-rays.¹ The tetrahedral arrangement of the bonds linking one carbon atom to its near neighbours was clearly demonstrated as early as 1913. There is a remarkable similarity between the structure of diamond and that of high or β -cristobalite as postulated by Wyckoff (cf. Fig. III.23B). In diamond, carbon atoms occupy the positions held by silicon in cristobalite, and there are, of course, no oxygen atoms. Each carbon atom is linked to four other similar atoms arranged at the corners of a regular tetrahedron. The bonding is wholly covalent as shown by the structure, hardness, brittleness, appearance and electrical resistance. Four of the eight corners of a cubelet in the cubic unit cell are occupied and by placing atoms at the centre of such cubelets every carbon atom can form four tetrahedral covalent bonds (see Fig. IV.1(a)).

The structure is based on a face-centred cube, but there are extra carbon atoms conferring cubic holosymmetry. The constants are given by W. H. and W. L. Bragg as

Diamond C	System: Cubic
Space Group (Mauguin): Fd 3m	Axis:
Number of atoms per unit cell = 8	$a = 3.56 \text{ \AA}$

The carbon to carbon distance in diamond is 1.54 \AA .

Graphite is a rather soft greyish material which occurs in nature as *graphite* or *plumbago* and artificially as coke and in some carbon electrodes. The contrast between the softness of graphite—which is used as a lubricant and for *black-leading*—and the hardness of diamond is very great.

¹ Bragg, W. H. and W. L., *Proc. Roy. Soc.*, A89, 277, 1913.

The carbon atoms in *graphite* are arranged in sheets and the atoms in each layer are nearly co-planar. The linking in graphite layers may be likened to that in the benzene ring C_6H_6 where the bonds between the carbon atoms are pictured as alternating double and single bonds with six atoms uniting to form a complete hexagonal ring. The modern view is that there is resonance and each link is about 50 per cent double-bond and consequently, in benzene the carbon to carbon distance is between that of $C-C$ (1.54 \AA) and that of $C=C$ (1.34 \AA), being 1.39 \AA . The remaining valency of each carbon atom in benzene is satisfied by a hydrogen.

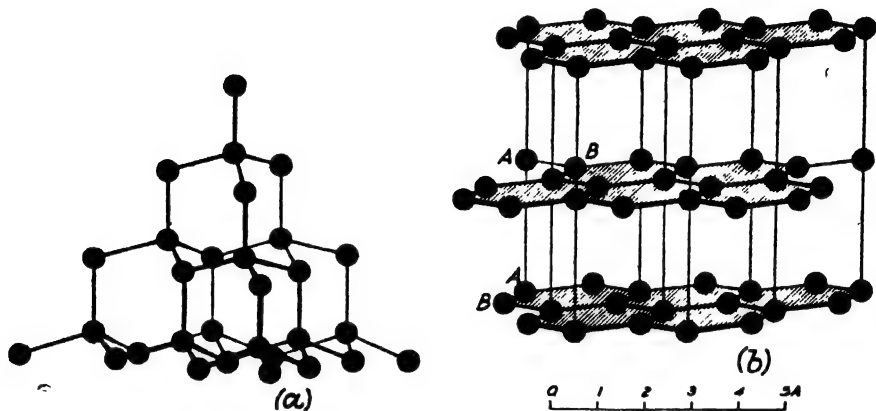
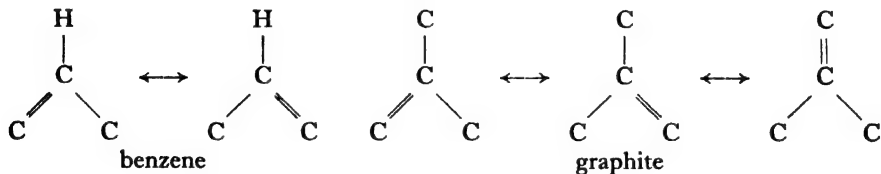


FIG. IV.1. THE CRYSTAL STRUCTURES OF (a) DIAMOND, AND (b) GRAPHITE

Graphite, on the other hand, consists of hexagonal carbon-linked rings extending indefinitely in two dimensions; so that any particular carbon atom is bound to two other similar atoms in the same ring and to another atom in an adjacent ring. Each atom resonates between three positions, thus:



It may be concluded that each bond in graphite has a third of a double-bond character and this is borne out by the increase in length of the carbon to carbon linkage to 1.42 \AA . The resonance energy strengthens the bonds and reduces the separation of the atoms to below that theoretically expected.

The bonding between the sheets is rather similar to that between the plates in montmorillonites. Van der Waal linkages have been suggested and the distance between each layer of carbon atoms is 3.40 \AA . The complete structure is given in Fig. IV.1(b).

Graphite has the following constants:¹

Graphite C	System: Hexagonal
Space Group: C6/mmc	Axes:
Z = 4	a = 2.46 Å
	c = 6.80 Å (i.e. two layers to one unit)

The similarity of graphite to montmorillonite is also seen on comparing their swelling properties. If graphite is treated with strongly oxidising agents such as potassium chlorate and nitric acid, the interlayer distance increases to between 6 and 11 Å. An oxide layer is most probably formed, as the expansion of the lattice may be related to the increase of combined oxygen. Molecules of water are also adsorbed between the layers. Sulphuric acid and fluorine have somewhat similar effects.

The linkages between the atoms in diamond have the characteristics of aliphatic compounds where carbon is in tetrahedral co-ordination; on the other hand, the bonding of the carbon atoms in graphite closely resembles that in aromatic compounds.

The black forms of carbon (e.g. soot and lampblack) including those produced by charring vegetable and other carbonaceous matter in clays are very different in appearance from commercial graphites, but they are composed of minute crystals of it and have a similar atomic structure. The chief structural difference is that in black carbon the distances between the layers are relatively larger than in coarser graphites and there is sometimes less regularity in the distribution of the atoms.

In many carbon blacks the carbon atoms are arranged regularly in hexagonal rings and the various planes are parallel in the *a*-direction but wholly random in the *c*-direction. Only after heating to 2800° C. are crystals of true graphite produced.

Some commercial graphites have crystals extending 50–100 Å in the *a*-direction and 20–50 Å in the *c*-dimension.

Carbon in the combined state occurs as:

(i) The *gases* carbon monoxide, CO, carbon dioxide, CO₂, acetylene, C₂H₂, methane, CH₄, etc.

(ii) Various *solid* and *liquid components*; those of chief interest in ceramics being (a) the *carbonaceous matter* (chiefly of vegetable origin) which occurs in clays, etc., and (b) various fuels such as coal, anthracite, coke and various oils.

The nature of the carbon in carbonaceous material associated with sedimentary clays is still largely conjectural. Much valuable and interesting work on the minerals in coals and shales has been carried out by Riley² who has suggested that small crystallites of graphitic-like minerals exist, which appear to be composed of sheets of co-planar carbon atoms alternating with undulating layers of complex groupings. There is little orientation in the stacking of layers and the interplanar distance is not constant. *Fusain* is a coal mineral with a structure resembling graphite and it is readily converted to true graphite on carbonisation at a moderately high temperature

¹ Lipson, H. and Stokes, A. R., *Nature*, 149, 328, 1942.

² Riley, H. L., *Quart. Reviews*, 1, 59, 1942.

under reducing conditions. *Clairain*, *vitrain* and *durain* are other minerals which contain a higher proportion of complex groupings.

Coke prepared at relatively low temperatures appears to be a mixture of amorphous carbon and graphite. Coke prepared at temperatures above 700° C. consists mainly of crystallites of graphite with a considerable proportion of border carbon atoms. On heating to about 1400° C. recrystallisation of the crystallites occurs; this is the basis of the Acheson method of making graphite from coke or anthracite. The chemical reactivity of coke is at a minimum when it is recrystallised into graphite.

Some clays contain a proportion of carbonaceous material in the form of algae or leaf remains in which the carbon molecules appear to have discrete existence.

OXIDES

MANY oxides are used as ceramic materials, as refractories, fluxes, opacifiers and colouring agents. The crystal structures of most of these have been accurately worked out and Wells¹ has given an excellent summary and classification of the main types.

TABLE IV—1. THE CRYSTAL STRUCTURE OF SOME OXIDES*
(after Wells)

<i>Co-ordination numbers of M and O and formula</i>	<i>Name of structure</i>	<i>Examples</i>
6:2 } MO_2	Fluorite	ReO_3 ThO_2 , CeO_2 , PrO_2 , UO_2 , (ZrO_2)
8:4 } MO_2		
6:3 } MO_2	Rutile	TiO_2 , VO_2 , MnO_2 , MoO_3 , WO_3 , etc.
4:2 } MO_2	Silica	
6:4 } M_2O_3	Corundum	$\alpha\text{-Al}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3$, Cr_2O_3 , V_2O_5 La_2O_3 , Ce_2O_3 , etc.
6:4 } M_2O_3	'A' rare-earth sesquioxides	
6:4 } M_2O_3	'C' rare-earth sesquioxides	Mn_2O_3 , and other rare earths
6:6 } MO	Rock-salt	
4:4 } MO	Wurtzite	MgO , CaO , BaO , FeO , etc. BeO , ZnO
4:8 } M_2O	Anti-fluorite	
4:8 } M_2O	Anti-fluorite	Li_2O , Na_2O , K_2O
Complex oxides		
ABO_3	Perovskite	CaTiO_3 , etc.
ABO_3	Ilmenite	FeTiO_3 , etc.
AB_2O_4	Spinel AB_2O_4	FeAl_2O_4 , ZnAl_2O_4 , etc.
	B(AB)O_4	FeMgFeO_4 , MgTiMgO_4

* All these structures are infinite three-dimensional complexes.

Although this table is an excellent guide to the relationships between the oxides, it must be remembered that the structures are idealised and represent the oxygen atoms in some form of close-packing, which they are certainly not in many instances. Furthermore, some oxides are capable of existing in more than one modification, each of different spacial arrangement. Certain oxides undergo transformations at high temperatures, thereby forming new modifications, which are

¹ Wells, A. F., *Quart. Reviews*, 2, 185, 1948.

often instantly reversible on cooling to normal temperature, yet in ceramic reactions it is sometimes the high-temperature form which is important, especially in the study of firing reactions.

The oxides, however, are conveniently arranged in order of type.

OXIDES MO

METALLIC oxides with the formula MO form two groups, depending on the different co-ordinations of the cations and oxygen ions.

(a) **With 6:6 co-ordination.** This group includes the alkaline earth oxides MgO, CaO, SrO, BaO, etc., along with the transitional metal oxides CdO, VO, MnO, FeO, CoO and NiO.

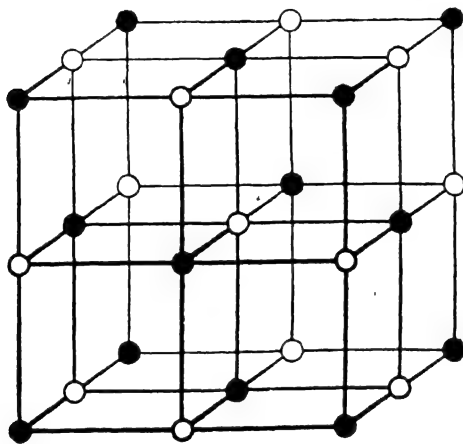


FIG. IV.2. THE PERICLASE STRUCTURE, BASED ON ROCK SALT
(Black dots represent cation, and circles, anion locations)

The structure of all oxides in this group is based on that of rock-salt, NaCl. Each cation is in six-fold co-ordination with oxygen atoms, each of which receives one-third of a valency share. As a consequence, all oxygen atoms must, in turn, be in contact with six cations. The structure of all oxides in this group is *cubic* with the corresponding cation and oxygen atoms occupying alternate corners of a set of cubes (see Fig. IV.2). The unit cell contains four groups of MO. The constants for periclase, MgO, are:

Periclase MgO
Space Group: Fm3m
 $Z = 4$

System: Cubic
Axis:
 $a = 4.20 \text{ \AA}$

Huber and Wagener¹ have listed the length of the unit cell of each oxide of the rock-salt type. It is interesting to compare these values with the size of the corresponding cation.

¹ Huber, H. and Wagener, S., *Z. tech. Physik.*, 23, 1, 1942.

TABLE IV—II. LATTICE CONSTANTS OF ALKALINE EARTH AND RELATED OXIDES

Oxide	Axis	Radius of cation	Oxide	Axis	Radius of cation
MgO	4.20 Å	0.78 Å	CdO	4.70 Å	1.03 Å
CaO	4.80	1.06	MnO	4.42	0.91
SrO	5.15	1.27	FeO	4.28	0.83
BaO	5.53	1.43	CoO	4.25	0.82
			NiO	4.17	0.78

The length of the unit cell in each instance is almost in direct ratio to the ionic size of the respective cation.

An unusual feature of the oxides of the *alkaline earth metals* is that only magnesia can form a stable crystal which is not liable to hydration when exposed to normal atmospheric conditions. No matter how lime, strontia or baria are heat-treated, it is impossible to convert them into a form with the permanent character of periclase. The answer lies partly, if not entirely, in the crystal configuration of these oxides. If reference is made to Table II.XIII (p. 84), the stable co-ordinations (calculated as the ratio of the cation/anion radii) of each alkaline earth metal with respect to oxygen may be compared. Magnesium is well within the limits of six-fold co-ordination, but calcium and, to an even greater extent, strontium and barium are too large. The resulting octahedral configuration of oxygens around each cation must, therefore, be highly distorted except in the case of magnesium. The close-packed idealised structure must be replaced by a more open structure, permitting the free access of water molecules and the consequent ease with which all alkaline earth oxides, except periclase, can be hydrated.

The *transitional group oxides* have ions of suitable sizes to conform to the requirements of six-fold co-ordination with oxygen. Cadmium is a little large and is the least resistant to hydration. The mineral FeO (*ferrous oxide* or *wustite*) is not very common in nature, but is considered to be the normal form of iron oxide at temperatures above 1200° C. *Wustite* very readily oxidises to the ferric form under normal conditions.

(b) **With 4:4 co-ordination.** Oxides of composition MO with this low co-ordination must be divalent and with cations of very small ionic radii; *beryllia*, BeO, is the only oxide of importance which conforms to this configuration, because beryllium has an ionic size of 0.34 Å. Each beryllium ion is surrounded by four oxygen atoms, which each require to be in contact with four metal ions to satisfy their valency requirements. The structure resembles that of *wurtzite*, ZnS, but the bonds are probably more covalent than in the alkaline earth oxides.

The constants of beryllia¹ are:

Beryllia BeO
Space Group: C6mc
Z = 2

System: Hexagonal
Axes:
a = 2.67 Å
c = 4.39 Å

¹ Nitka, H., *Nature*, 29, 336, 1941.

and the structure of wurtzite is shown in Fig. IV.3; in beryllia, beryllium ions replace the zinc, and oxygen the sulphur in the wurtzite structure.

In oxides of the beryllia type, the oxygen atoms are ideally hexagonally close-packed. The metallic cations occupy all vacant lattice sites and the sequence of layers is ABABAB, etc. Magnesium oxide is also close-packed but of the cubic type with layers ABCABC, etc., and all vacant lattice sites are also occupied by cations.

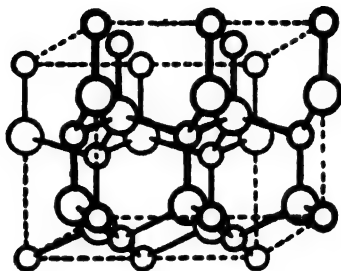


FIG. IV.3. THE STRUCTURE OF BERYLLIA (BASED ON WURTZITE)
(Small circles represent the cations, larger circles the anions)

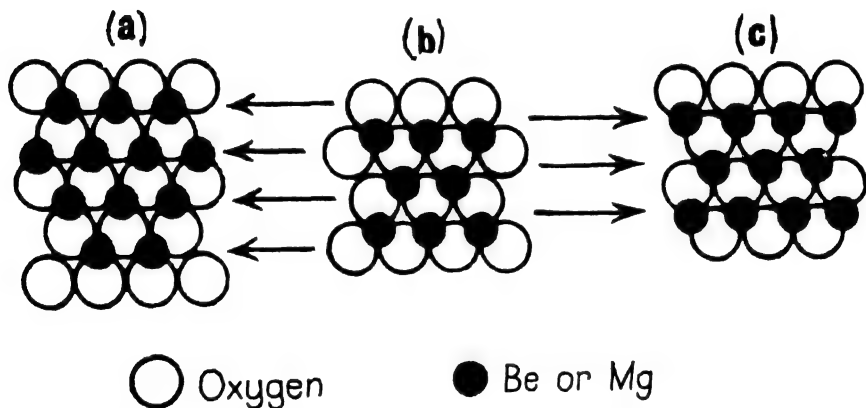


FIG. IV.4. A COMPARISON OF THE STRUCTURES OF MAGNESIA AND BERYLLIA
(b) superimposed on (a) gives beryllia; (b) superimposed on (c) gives magnesia.

The comparison between these two structures is demonstrated in Fig. IV.4. If the centre unit (b) is moved to the left above unit (a) until each oxygen is directly over a cation, then the structure of beryllia results. If the (b) unit is moved to the right until a cation in unit (c) lies immediately below the vacant lattice site between three oxygens in unit (b), then the periclase structure is produced. The third layer of oxygen atoms must then be arranged to give four-fold co-ordination in the beryllia structure, and six-fold in the periclase. Hexagonal and cubic close-packing are the respective configurations.

Zinc oxide (ZnO) has a similar structure to beryllia although the tetrahedral bonding is probably more covalent.

(c) **Other forms of MO minerals.** Compounds are known where the composition corresponds with the general formula MO, but where simple co-ordinations are not present.

Lead oxide (PbO) is thought to exist in three forms, (a) tetragonal, (b) orthorhombic, and (c) monoclinic, but only the structure of the first has been established with certainty. Each lead atom is linked to four oxygen atoms, but these all lie to one side of the cation and are each linked to two lead atoms and receive a valency share from each. Layers of such linkages are built up and are linked to other similar layers by bonds, the nature of which has not been established.¹

Cupric oxide (CuO) has a structure in which each copper atom is linked to four co-planar oxygen atoms.²

OXIDES M_2O_3

THIS group includes those compounds which have long been known as the sesquioxides. Wells has suggested that there are three separate sections with distinct structures.

(i) **The 'A' group of rare earth sesquioxides** is of small importance in ceramics, and includes *lanthana* and *ceria*. These are unusual in that the metal cation is co-ordinated with seven oxygen ions.

(ii) **The 'C' group of rare earth sesquioxides** has a structure resembling *fluorite*, CaF_2 (see p. 191), with the cations in six-fold co-ordination but not in a simple manner. Many rare earth oxides have this structure and *lanthana* if crystallised at a high temperature will take this form. *Manganese trioxide*, Mn_2O_3 , which is an important colouring agent for domestic ware has this structure.

(iii) **The corundum group** is the most important in ceramics, for in addition to α -*alumina*, it includes *hematite* (α - Fe_2O_3), *chromic oxide* (Cr_2O_3), and the *sesquioxides of titanium* (Ti_2O_3), and *vanadium* (V_2O_3).

Corundum (α - Al_2O_3) has been analysed by W. H. and W. L. Bragg,³ and by Pauling and Hendricks.⁴ Its crystal form is rhombohedral with constants of:

Corundum Al_2O_3
Space Group: $R\bar{3}c$
 $Z = 2$

System: Rhombohedral
Axis: $a = 5.12 \text{ \AA}$
Angle: $\alpha = 55^\circ 17'$

The structure consists of layers of oxygen atoms arranged in hexagonal close-packing. Each aluminium atom is surrounded by six oxygens. The valency contribution to each co-ordinating anion is one-half, so that each oxygen must be linked to four cations. If all possible positions were filled by aluminium atoms there would be as many cations as anions, as in periclase, and each oxygen would be receiving three valency shares—a half from each of six cations. Only two-thirds of the available octahedral lattice sites are in fact filled by aluminium and the structure

¹ W. J. Moore and L. Pauling, *J.A.C.S.*, **63**, 1392, 1941.

² G. Tunell, E. Posnjak and C. J. Ksanda, *Zeit Krist.*, **90**, 120, 1935.

³ Bragg, W. H. and W. L., *X-rays and Crystal Structure* (Ball and Sons, 1916).

⁴ Pauling, L. and Hendricks, S. B., *J. Amer. Chem. Soc.*, **47**, 781, 1925.

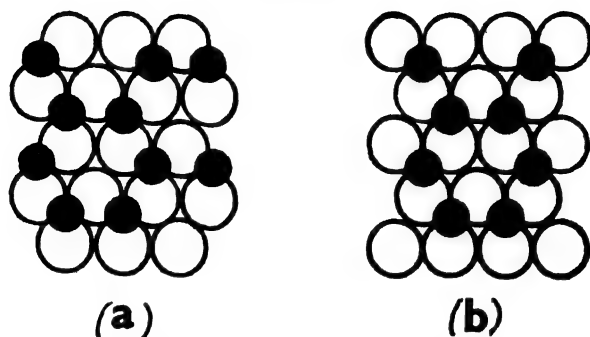


FIG. IV.5. THE STRUCTURE OF CORUNDUM
Unit (b) is superimposed on (a) and the progression
of layers is ababab, etc.

is electrically balanced. The idealised form of packing of two oxygen layers is shown in Fig. IV.5; the third layer is immediately above the first.

The dimensions of other minerals which have a similar configuration are tabulated below:

TABLE IV—III. LATTICE CONSTANTS OF THE
CORUNDUM GROUP

		Space group	Axis <i>a</i>	Angle α	Radius of cation
Corundum*	Al ₂ O ₃	R3c	5.118 Å	55° 17'	0.57 Å
Chromic oxide*	Cr ₂ O ₃	—	5.351	55° 06'	0.64
Hæmatite	Fe ₂ O ₃	—	5.420	55° 17'	0.67
Ilmenite†	(Fe,Mg)TiO ₃	R3̄(C ₃ ^v)	5.400	55° 01'	—

* Jay, A. H. and Wild, W. T., *Min. Mag.*, 27, 56, 1944.

† Ilmenite is structurally similar, but the introduction of two different cations destroys the symmetry of the space group and results in one of lower order.

Aluminium oxide is known to exist in other crystal modifications, viz. γ - and β -alumina: γ -alumina may be prepared by heating any hydrated aluminium oxide to 200–500° C. at which temperature it loses water of crystallisation and produces small crystallites of γ -alumina. This mineral is also a decomposition product of many clays and similar materials. The crystal structure is cubic with a lattice parameter of $a=7.88$ Å. Aluminium ions are in both four- and six-fold co-ordination in what is apparently a defect spinel lattice (see p. 195) with $21\frac{1}{3}$ metal ions in a unit cell as against a normal 24.

The effect of heat on this form is most interesting; Rooksby¹ has identified at least two other modifications by maintaining the crystal between 600 and 950° C. for long periods of time. The crystallite size increases under these conditions and the

¹ See *X-ray Identification and Crystal Structures of Clay Minerals* (Mineralogical Society, London, 1951), p. 250.

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³ Bragg, W. H. and W. L., *X-rays and Crystal Structure* (Ball and Sons, 1916).

⁴ Pauling, L. and Hendricks, S. B., *J. Amer. Chem. Soc.*, **47**, 781, 1925.

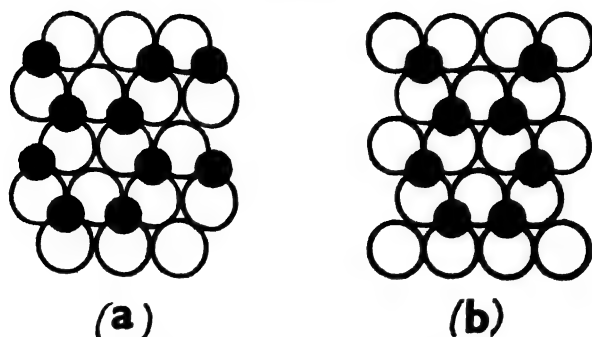


FIG. IV.5. THE STRUCTURE OF CORUNDUM
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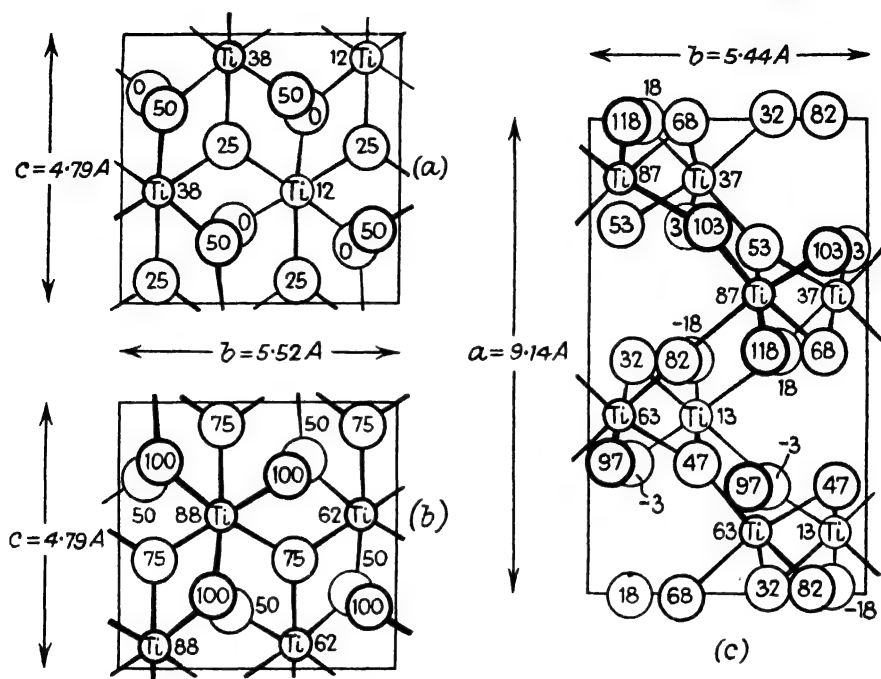


FIG. IV.7. THE STRUCTURE OF BROOKITE
(after Pauling and Sturdivant)

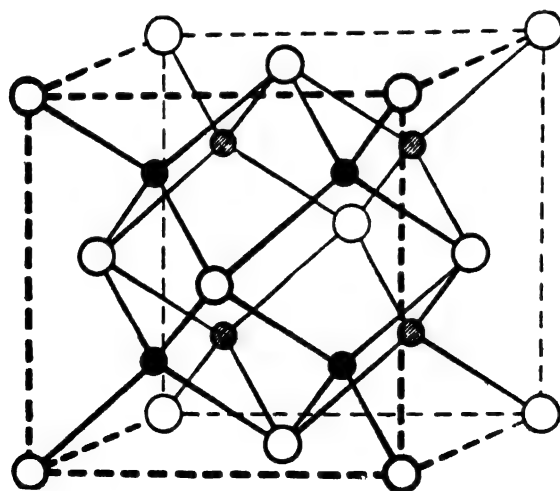


FIG. IV.8. THE STRUCTURE OF FLUORITE
(after Bragg)

Shaded circles are cations, open circles are anions.

(b) **MO₂ with 8:4 co-ordination.** When quadrivalent cations are too large for six-fold co-ordination, the surrounding oxygens are arranged in the form of a cube; thus the cation is in eight-fold co-ordination. Each oxygen receives a half valency share from the cations with which it is in contact and consequently requires to touch four.

The type-structure of this group of oxides is the mineral *fluorite*, CaF₂, which is based on a face-centred cube, and shown in Fig. IV.8. The oxides of thorium, cerium, uranium and zirconium are of similar structure with oxygen replacing fluorine, and the metallic ion replacing calcium.

Zirconia (*baddeleyite*) occupies an anomalous position, for it has a monoclinic structure which is really a distorted form of the fluorite structure.

When the cationic radius and the cation/oxygen size ratio of some of these quadrivalent elements are compared, very interesting facts emerge (see Table IV.V).

TABLE IV—V. DEPENDENCE OF STRUCTURE ON CATIONIC SIZE OF THE OXIDES RO₂

Cation	Radius	Cation/oxygen radius ratio	Co-ordination No.	Type of structure of oxide	
Titanium	0.64 Å	0.485	6	Rutile.	Tetragonal
Tungsten	0.68	0.516	6	"	"
Tin	0.74	0.560	6	"	"
Zirconium	0.87	0.660	6 (8)	Distorted fluorite.	Monoclinic
Uranium	1.05	0.796	8	Fluorite.	Cubic
Thorium	1.10	0.832	8	"	"
Cerium	1.18	0.894	8	"	"

The *titanium*, *tin* and *tungsten* cations fall well within the size range for six-fold co-ordination with oxygen, whilst the *cerium*, *thorium* and *uranium* cations are within the eight-fold range. The *zirconium* cation falls almost on the borderline of the two groups. It might, therefore, be expected to fall in either class, or to form a distorted grouping of one of them, which, in fact, it does. At high temperatures pure zirconia is transformed into a tetragonal structure; the zirconium ion presumably increases in size less than the oxygen anion, and the cation/anion ratio falls into the stable six-fold co-ordination range of rutile. On cooling, the mineral reverts to the monoclinic form, but if it is fired to high temperatures with other oxides, it becomes stabilised in a cubic modification resembling fluorite.

Ruff and Ebert¹ originally reported that cerium oxide was the most effective stabilising oxide. Crystallographically, this is to be expected, for the fluorite structure of this oxide would 'seed' the crystallisation of a cubic zirconia. Geller and Favorsky,² however, have investigated the stabilising effect of other oxides and report that the alkaline earth oxides are superior even to ceria. Solid solution may occur and the combined effect is to produce a stable cubic form. The packing in the cubic

¹ Ruff, O. and Ebert, F., *Z. anorg. Chem.*, **180**, 19, 1929.

² Geller, R. F. and Favorsky, P., *J. Res. Nat. Bur. Standards*, **35**, 87, 1945.

type of zirconia will be very tight and would account for the high coefficient of thermal expansion observed in the stabilised form.

(c) **M₂O with 4:8 co-ordination.** Minerals with this configuration include the alkali oxides Li₂O, Na₂O and K₂O. The structure is similar to that of fluorite, but with the cation and anion positions reversed, the alkali metals occupying the F positions and the oxygen atoms the Ca positions. The structure-type is therefore called *anti-fluorite*.

(d) **The cuprite M₂O Group with 2:4 co-ordination** contains *cuprous oxide*, Cu₂O, and *argentum oxide*, Ag₂O. Both these oxides have a structure quite different from that of the anti-fluorite one (c), in consisting of two completely penetrating and identical frameworks which are not crossed by any primary M—O bonds.¹

OXIDES MO₃

THE simple cubic ReO₃ structure is related to that of perovskite (p. 196) with large (A) ions and O²⁻ ions forming a close-packed lattice with the smaller (B) ions in the interstices.

According to Wells,² the structures of CrO₃ and WO₃ are only slightly distorted versions of the ReO₃ structure.

OXIDES M₃O₄

IN this small group four oxides are of ceramic interest—*red lead*, Pb₃O₄, *magnetite*, Fe₃O₄, *cobalt tetroxide*, Co₃O₄, and *manganese tetroxide*, Mn₃O₄.

Red lead is usually a mixture of several lead oxides with an average composition corresponding to Pb₃O₄ so that no single crystalline structure can be assigned to commercial red lead. The pure tetroxide consists of PbO₆ octahedra sharing opposite edges and linked by Pb atoms each with a pyramidal arrangement of three oxygen atoms. According to Wells,¹ the constants are:

System:	Bond lengths:	Angles:
Octahedral	Pb ⁴⁺ O 6 at 2.15 Å	2 of 95.3°
	Pb ²⁺ O { 2 at 2.23 Å	1 of 91°
	1 at 2.15 Å	

Several mixed oxides have the same structure.

Magnetite, Fe₃O₄, is included among the Complex Oxides (p. 195).

Cobalt tetroxide is obtained by calcining cobaltous oxide and is the essential constituent of *prepared cobalt*—one of the most extensively-used potters' colours.

Manganese tetroxide, Mn₃O₄, is the *calcined manganese* used as a colouring agent by potters. Like other M₃O₄ oxides it contains the metal in two different states of valency and corresponds to the AB₂O₄ formula for complex oxides except that in the case of the four above-mentioned oxides the A and B elements are the same and could be written AA₂O₄, though this would not so clearly show that they are of different valencies.

¹ A. F. Wells, *Structural Inorganic Chemistry*, 2nd ed. (Clarendon Press, Oxford, 1950).

² Ibid.

COMPLEX OXIDE STRUCTURES

WELLS states that complex oxide structures of the general formula $A_xB_yO_n$ may be of three types:

- (a) where one ion (B) simply replaces another (A) without affecting the spacial configuration;
- (b) where blocks of oxides are joined by other cations; and
- (c) where complete new units are formed unlike any of the component oxides in the structure.

Type (a) requires little description, and is best represented by the mineral *ilmenite*, $(\text{FeMg})\text{TiO}_3$. The basic structure is *hamatite* ($\alpha\text{-Fe}_2\text{O}_3$), which is structurally similar to *corundum*. Titanium ions (Ti^{3+}) replace ferric ions in the lattice, for they are of comparable size and valency. There may be further replacement of iron by magnesium, for many ilmenites contain this element. MgTiO_3 , MnTiO_3 , CoTiO_3 and NiTiO_3 are all isomorphous with hamatite.

Type (b) includes many compounds composed of blocks of a simple structure linked by ions of other types. In this group, of importance in ceramic studies, is β -alumina and possibly γ -alumina, and $\gamma\text{-Fe}_2\text{O}_3$. In the former, the structure is composed of blocks of a spinel type, linked together through alkali ions. They can be studied as an adjunct to the last group.

Type (c), where new structure types are formed, includes the important group of minerals—the *spinel*s. The well-known form of spinel—the gem-stone $\text{MgO} \cdot \text{Al}_2\text{O}_3$ was first analysed by W. H. Bragg¹ and by Nishikawa,² and shown to have a cubic structure. Other workers have identified minerals of variable composition in this group, and it is now customary to write the spinel form in general terms $\text{R}^{2+}\text{O} \cdot \text{R}_2^{3+}\text{O}_3$ where R^{2+} is a divalent cation, such as Mn, Mg, Fe^{2+} , etc., and R^{3+} is a trivalent cation such as Al, Fe^{3+} , Cr, etc. The chrome ores, for example, contain a high proportion of spinel where the trivalent cation is chromium; these ores are used extensively in the manufacture of basic refractories (see Chapter VI).

The structure of all spinels is based on a unit cell of 56 atoms including 32 oxygen atoms arranged in cubic close-packing. In the interstices between the oxygen atoms are two types of cations, 8 of which are in four-fold co-ordination and 16 in six-fold co-ordination (see Fig. IV.9). There are essentially two different cation/oxygen layers, the first (a) with a close-packed layer of oxygen atoms and cations of four- and six-fold co-ordination. The second layer (b) is also a close-packed layer, but with six-fold cations only; if (b) is moved directly to the right until the points XX and YY coincide, the arrangement of atoms in the first two layers is produced. The third layer (c) is like the first, but to satisfy the co-ordination requirements of cations B it has to be stacked in such a way that cubic close-packing results. This may be shown by moving unit (c) directly over the superposed (a) and (b) units so that XXX and YYY now lie immediately above each other.

The formula of a spinel may be represented by the general formula AB_2O_4 , i.e. it contains twice as many B atoms as A atoms. Therefore it is logical to place the

¹ Bragg, W. H., *Phil. Mag.*, 30, 305, 1915.

² Nishikawa, S., *Proc. Tokyo Math. Phys. Soc.*, 8, 199, 1915.

A atoms in the eight tetragonal or four-fold co-ordinated groups, and the B atoms in the sixteen octahedral or six-fold co-ordinated groups. Barth and Posnjak¹ showed, by careful measurement of the X-ray line-intensities of certain spinels, that there could be an alternative arrangement whereby eight B-type atoms occupy the tetrahedral positions and the octahedral positions are filled by eight A type and eight further atoms of the B type, randomly arranged. This leads to two general formulæ: Group 1 or *normal* spinels represented by AB_2O_4 , and Group 2 or *inverse* spinels represented by $B(AB)O_4$.

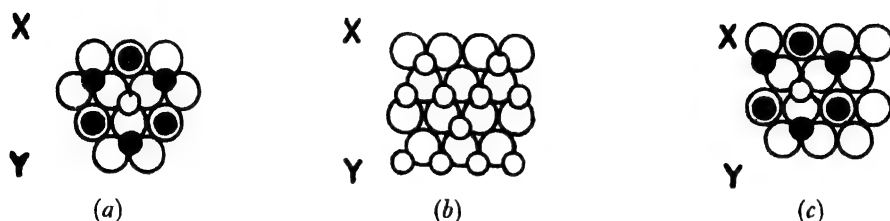


FIG. IV.9. THE STRUCTURE OF SPINELS

Small open circles represent cations in octahedral co-ordination. Small black circles represent cations in tetrahedral co-ordination, large circles represent oxygen ions.

The structure is obtained by moving (b) on to (a) and then (c) on to (b) in such a way that the points X and Y are superimposed.

Group 1 spinels include those with the A atoms Fe^{2+} , Co, Ni, Mn and Zn, whereas the inverse type, Group 2, is usual when ferric iron is present.

The structure constants for the spinel gemstone $MgAl_2O_4$ is:

Spinel $MgAl_2O_4$
Space Group: $Fd\bar{3}m$
 $Z = 8$

System: Cubic
Axis:
 $a = 8.10 \text{ \AA}$

The types of spinel associated with chrome ore will be considered in more detail in Chapter VI, but the wide range in chemical composition of this group may be judged from the following table.

TABLE IV-VI. SOME MINERALS WITH SPINEL STRUCTURE

Name	Chemical Composition	Length of Unit Cell
Spinel	$MgAl_2O_4$	8.07 Å
Gahnite	$ZnAl_2O_4$	8.075
Hercynite	$FeAl_2O_4$	8.115
Chromite	$FeCr_2O_4$	8.346
Picrochromite	$MgCr_2O_4$	8.308
Magnesioferrite	$MgFe_2O_4$	8.368
Magnetite	$FeFe_2O_4$	8.38

These minerals represent end-members of the spinel group, for extensive solid solution may occur between all of them.

¹ Barth, F. W. and Posnjak, E., *Zeit. Krist.*, **82**, 325, 1932.

It is probable that only the last two, *magnesioferrite* and *magnetite*, belong to Group 2 and have the inverse structure, although some doubt is attached to spinel MgAl_2O_4 itself. The unit cell parameter figures shown are the mean of values obtained by several workers.

More detailed consideration must be given to the spinel structures of gamma (γ)-alumina Al_2O_3 , gamma (γ)- Fe_2O_3 and magnetite Fe_3O_4 .

Magnetite, Fe_3O_4 , is a true spinel, for in a unit cell there are 32 cubic close-packed oxygen atoms and 24 cations, 8 of which are in the ferrous form and 16 ferric ions. The structure may then be written as $\text{Fe}^{2+}\text{Fe}_2^{3+}\text{O}_4$ or better still, for it is an inverted form, as $\text{Fe}^{3+}\text{Fe}^{2+}\text{Fe}^{3+}\text{O}_4$. Gamma (γ)- Fe_2O_3 has only $21\frac{1}{3}$ cations to a unit cell and all of these are in the ferric form distributed in a random fashion throughout the 24 available lattice sites. Wells¹ has made a careful study of the relationships between FeO , Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$. The former mineral also is built up of oxygens in cubic close-packing configuration, but there are as many ferrous ions as oxygens; it may be considered as the extreme end of the series with 32 oxygen and 32 iron ions all of which are in the ferrous form. The oxidation of ferrous oxide, FeO , to magnetite, Fe_3O_4 , may be visualised as the addition of extra layers of oxygens and the migration of some cations to new lattice sites making the ratio of O^{2-} to Fe ions 32:24, and two-thirds of the iron is as Fe^{3+} . Further oxidation results in a continuation of this process until the oxygen:iron ratio is 32: $21\frac{1}{3}$ and all the iron is as Fe^{3+} .

In the spinel structure of Fe_3O_4 , Fe^{2+} and Fe^{3+} ions are distributed over a few octahedral and tetrahedral voids whereas in $\gamma\text{-Fe}_2\text{O}_3$ the Fe^{3+} ions are distributed at random over eight-ninths of the spinel positions.

The large series of solid solutions between Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ can be regarded either as Fe_3O_4 with an oxygen excess or as $\gamma\text{-Fe}_2\text{O}_3$ with an excess of metal.

γ -alumina has a similar structure to $\gamma\text{-Fe}_2\text{O}_3$, but with aluminium cations in place of ferric iron.

Gamma iron oxide and gamma alumina, are not very stable and are readily converted into haematite or corundum respectively; both can be stabilised, however, by the addition of ions such as lithium, and it may be that in these forms the alkali ions act as a bridge between structural blocks. This is the case in *beta* (β)-*alumina*, which has the chemical composition $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$. Beevers and Ross, showed that it is composed of spinel units, linked together through sodium ions with aluminium in both four- and six-fold co-ordination. The lattice constants are:

β -alumina $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$
Space Group: C6/mmc
Z = 2

System: Hexagonal
Axes:
a = 5.584 Å
c = 22.45 Å

A structural representation is given in Fig. IV.10. The mineral may also be prepared with potassium replacing sodium as the 'bridging' ions for the spinel units.

Another type of complex oxide structure of increasing importance in ceramics is the group typified by the mineral *perovskite*, $\text{CaO} \cdot \text{TiO}_2$. Large cations can be associated with oxygen in forming a close-packed structure; such ions, e.g. Sr, Ba,

¹ Ibid., p. 192.

K and Na, will then be in twelve-fold co-ordination. Smaller cations occupy positions of four- or six-fold grouping to form complex structures, which include some *tungstates* and *molybdates*, e.g. NaWO_3 . *Barium titanate*, which has valuable electrical properties, is of this structure and Goldschmidt and Rait¹ suggest that *merwinite*, $3\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$, may be of this type.

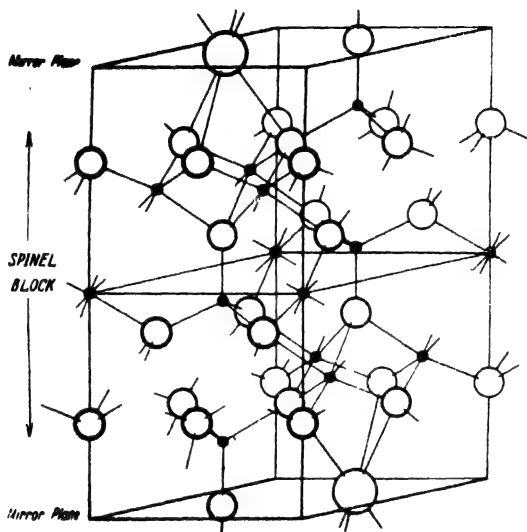


FIG. IV.10. THE STRUCTURE OF β -ALUMINA
(after Bevers and Ross)

Where cations of variable valency are present in a compound, there is the possibility of complex structures; in some instances a simple chemical formula disguises a complicated configuration.

Chrysoberyl, BeAl_2O_4 , is of similar composition to the spinels, but is structurally different. The oxygens in this case are hexagonally close-packed and the structural constants are:

Chrysoberyl BeAl_2O_4
Space Group: Pbmn
 $Z = 4$

System: Orthorhombic

Axes:

$a = 4.24 \text{ \AA}$

$b = 9.39 \text{ \AA}$

$c = 5.47 \text{ \AA}$

Cobalt oxide, Co_3O_4 , is also a spinel, but is very often impure, like chromite, as the result of replacements.

HYDROXIDES

IN order to understand the structure of the important hydroxides it is necessary to have a clear idea of the unusual features of the linkage in hydroxyl (OH) groups.

¹ Goldschmidt, H. J. and Rait, J. R., *Nature*, 152, 356, 1943.

This is all the more necessary because the simple hydroxides range from strongly basic and alkaline compounds such as caustic soda, NaOH, through the amphoteric hydroxides, such as $\text{Al}(\text{OH})_3$, to the hydroxy-acids of boron, phosphorus, silicon, etc.

The oxygen atom has six electrons in the outermost orbit (p. 68). If a hydroxyl unit is formed, one electron is added to the oxygen orbit and the eighth can be acquired either by forming a covalent linkage, ($-\text{O}-\text{H}$), or by acquiring an electron from a metal element and forming an ion which will be the hydroxyl or $(\text{OH})^-$ anion.

The hydrogen atom is very small compared with oxygen and consequently the hydroxyl ion can be imagined as a sphere of similar size to an oxygen ion, but of only unit negative charge.

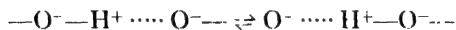
The greater the difference in electronegativity between the atoms forming a linkage, the greater will be the degree of ionic bonding (see p. 78). Consequently alkali atoms such as sodium, potassium, etc., will be linked largely in ionic fashion to hydroxyl units and molecules of this type may be represented by $\text{M}^+(\text{OH})^-$.

As the difference in electronegativity becomes less, the ionic nature of the linkage decreases through the amphoteric hydroxides like Al and Fe to the hydroxy-acids of B, P, and Si. In these latter elements the covalent union of oxygen is so strong that the hydrogen can be *ionised* (i.e. split up into separate ions) and an acid complex formed, thus:



Boric, phosphoric and silicic acids are of this type.

When these principles are applied to the arrangement within a crystal lattice, there can be two types of bonds: (i) the hydroxyl- $(\text{OH})^-$ ion can behave as a rigid sphere and form close-packed ionic-linked structures rather similar to the oxides, or (ii) covalently bonded atoms may have the distorted configuration of complex ions (see p. 87), with the hydroxyl unit behaving as a dipole (p. 77). Other negatively-charged oxygen ions in the vicinity can influence the dipole and attract the hydrogen ion, thereby setting up the resonance structure (see p. 75):



which represents a 'hybrid' of two states of equal energy. Most bonds are intermediate between the extremes of ionic and covalent types, consequently intermediate types of hydroxyl linkages may be expected.

The alkaline earth hydroxides are examples of hydroxyl bonding which is virtually ionic in character:

Magnesium hydroxide (brucite, $\text{Mg}(\text{OH})_2$) has a layer-lattice structure with hydroxyl units in positions of hexagonal close-packing with the Mg ions in octahedral co-ordination and each OH ion linked to three Mg cations. Each layer consists of two sheets of OH groups with a layer of magnesium atoms between, arranged so that each cation is in contact with six larger ions. Another exactly similar layer lies above the first situated in such a way that all OH groups in it touch three identical groups in the layer beneath. Because each layer is electrically balanced there can only be weak secondary forces between opposed OH layers and these hold the

structure together. Aminoff¹ was the first to determine the atomic configuration of brucite and the constants are:

Brucite $\text{Mg}(\text{OH})_2$
Space Group: $C-3m$
 $Z = 1$

System: Hexagonal (alternating)
Axes:
 $a = 3.12 \text{ \AA}$
 $c = 4.73 \text{ \AA}$

The structural features can be seen in Fig. IV.11; (a) shows the configuration of $(\text{OH})^-$ and Mg^{2+} ions in one layer and (b) the packing of hydroxyl units between adjacent layers.

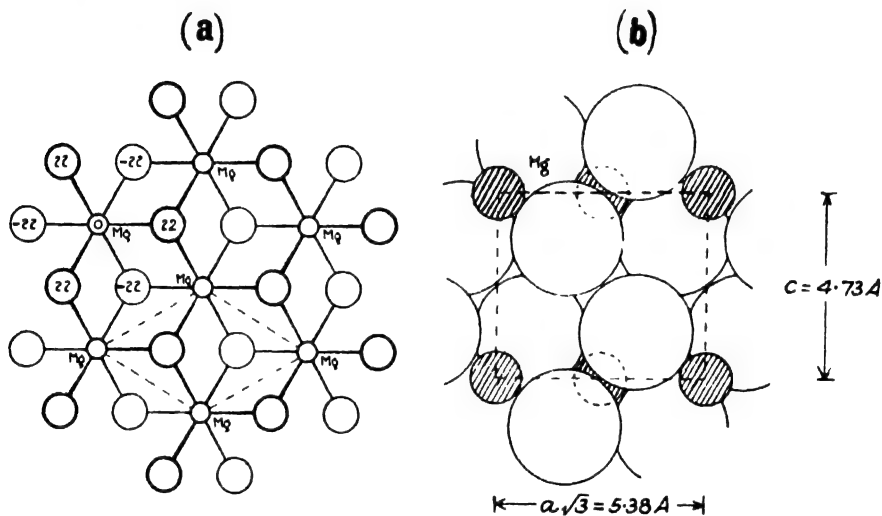


FIG. IV.11. THE STRUCTURE OF BRUCITE, $\text{Mg}(\text{OH})_2$,
(after Megaw)

(a) Schematic; (b) the relative position of atoms in adjacent layers.

Aluminium hydroxide, $\text{Al}(\text{OH})_3$, is known as *gibbsite* or *hydrargillite* and unlike brucite is not basic, but *amphoteric*, i.e. it may be weakly electronegative (acid) or electropositive (basic) under certain conditions.

The hydroxyl groups are not entirely ionic and non-directed but are slightly polar as a result of the dipole caused by the greater degree of covalency in the bonding. This structure is made up of layers composed of two close-packed hydroxyl sheets with aluminium atoms lying in six-fold co-ordination between them. Aluminium is trivalent, therefore only two-thirds of the possible vacant lattice sites are occupied. The essential difference between gibbsite and brucite lies in the relative stacking of adjacent layers. The hydroxyl groups in the gibbsite structure are sufficiently polar to exert an attractive force on others in the immediate vicinity and as a result each OH group lies directly over another in the adjacent layer. It is

¹ Aminoff, G., *Geol. Fören. Föhr. Stock.*, 41, 407, 1919.

postulated¹ that hydroxyl bonds link up the individual OH groups which are in contact. The structural constants are:

Hydrargillite or gibbsite $\text{Al}(\text{OH})_3$
 Space Group: $P2_1/n$
 $Z = 8$

System: Monoclinic
 Axes: Angle:
 $a = 8.624 \text{ \AA}$
 $b = 5.060 \text{ \AA}$ $\beta = 85^\circ 26'$
 $c = 9.699 \text{ \AA}$

and the idealised atomic arrangements are illustrated in Fig. IV.12 and may be compared with brucite.

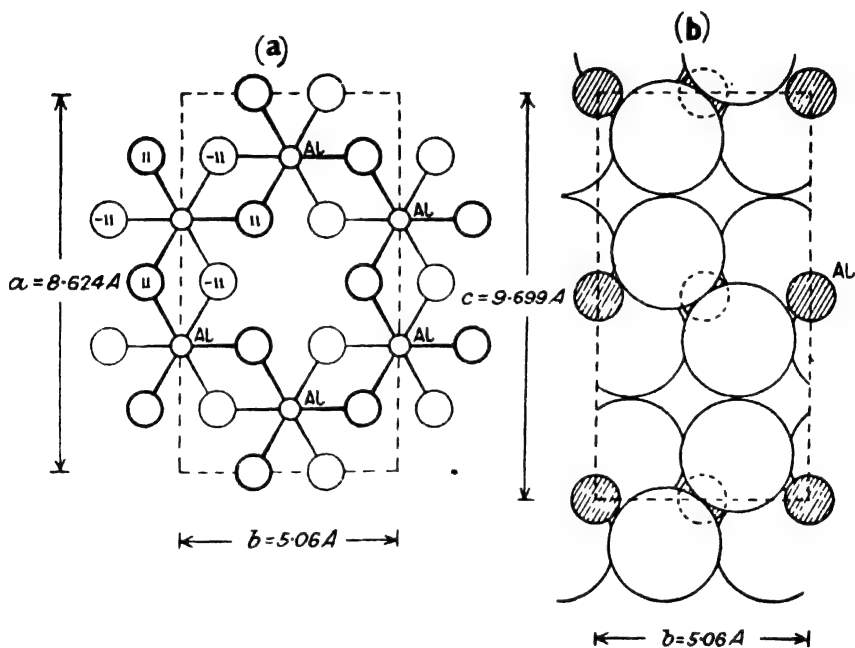


FIG. IV.12. THE STRUCTURE OF GIBBSITE, $\text{Al}(\text{OH})_3$
 (after Megaw)

(a) Schematic; (b) the relative positions of atoms in adjacent layers.

Gibbsite is a naturally-occurring mineral, but when the tri-hydrate of alumina is prepared artificially by precipitation from a salt, the resulting form, *bayerite*, has a rather different atomic configuration. The structure has been described by Montoro² as having hexagonal symmetry.

The hydroxide of *beryllium* is similar to gibbsite but all available octahedral positions in the lattice have to be filled, because the cation is divalent.

■ The extreme (acid) end of the hydroxyl series is typified by *boric acid*, H_3BO_3 . The structure appears to consist of discrete molecules of $\text{B}(\text{OH})_3$ linked to each

¹ Megaw, H. D., *Zeit. Krist.*, 87, 185, 1934.

² Montoro, V., *Ricerca Sci.*, 13, 565, 1942.

other through hydroxyl bonds ($\text{—O}\cdots\text{H}\cdots\text{O}$). A figurative representation is given in Fig. IV.13. *Silicic acid* may have a similar configuration.

As the nature of the bonding in the hydroxyl group decreases from the ionic, non-polar, non-directed unit to the dipole type of covalent linkage so does the distance decrease between adjacent oxygen atoms. As in graphite, when resonance occurs between two systems, the bond length is shortened and this may be illustrated by the series $\text{Mg}(\text{OH})_2\text{—Al}(\text{OH})_3\text{—B}(\text{OH})_3$. In the former the OH—OH distance is 3.22 \AA ; in gibbsite with some OH bonding it is 2.78 \AA ; and in boric acid where the linkages are $\text{—O}\cdots\text{H}\cdots\text{O—}$ the distance is 2.70 \AA .

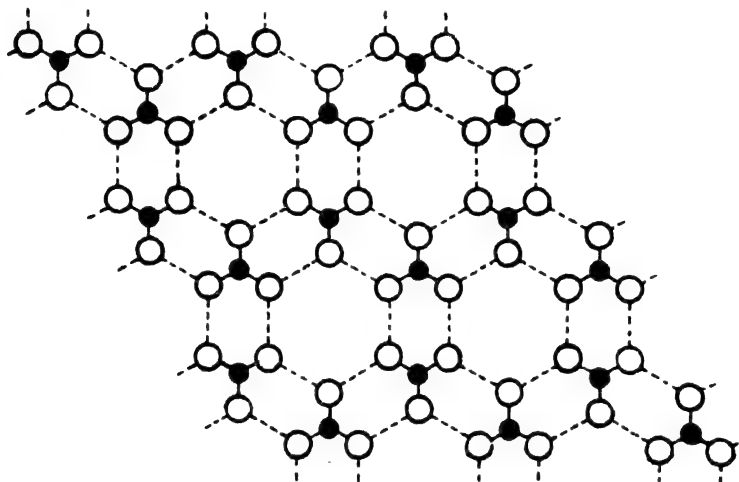


FIG. IV.13. THE STRUCTURE OF BORIC ACID

OXY-HYDROXIDES

SOME trivalent metals form hydroxides which are intermediate between the type $\text{M}(\text{OH})_3$ and the fully dehydrated oxide M_2O_3 . These compounds, which have the general formula $\text{MO}(\text{OH})_n$, are termed *oxy-hydroxides*. The oxy-hydroxides of aluminium and iron are isodimorphous, i.e. they are capable of existing in two forms as follows:

Diaspore $\alpha\text{-AlO.OH}$

Boehmite $\gamma\text{-AlO.OH}$

Goethite $\alpha\text{-FeO.OH}$

Lepidocrocite $\gamma\text{-FeO.OH}$

The structure of *diaspore* has been deduced by Takané¹ and Deflandre;² it is based on hexagonal close-packing of oxygens, with aluminium atoms lying between six oxygen atoms and every oxygen touching three cations. The contribution which each anion receives from the aluminium atoms in contact with it, is therefore three half valencies. The structure can be electrically balanced only if the hydrogen atom

¹ Takané, K., *Proc. Imp. Acad. Tokyo*, 9, 113, 1933.

² Deflandre, M., *Bull. Soc. Franc. Min.*, 55, 140, 1932.

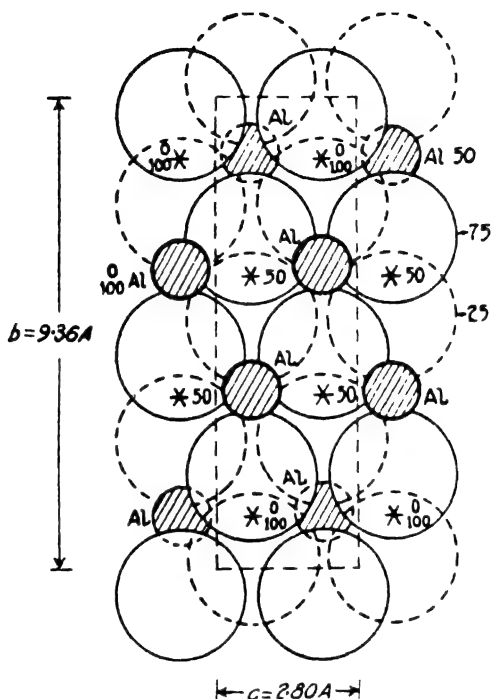


FIG. IV.14. THE STRUCTURE OF DIASPORE AND GOETHITE
(after Bragg)

indicated by an asterisk behaves as a small cation with planar configuration between two oxygens, thus donating a half-valency share to each. The structure is illustrated in Fig. IV.14, and the constants are:

Diaspore HAlO_2
Space Group: Pbnm
 $Z = 4$

System: Orthorhombic

Axes:

$a = 4.43 \text{ \AA}$

$b = 9.36 \text{ \AA}$

$c = 2.80 \text{ \AA}$

Goethite is of similar structure but with dimensions of $a = 4.54 \text{ \AA}$; $b = 10.0 \text{ \AA}$; and $c = 3.03 \text{ \AA}$.

Boehmite and *lepidocrocite* have a different configuration from the α -modifications but are similar to each other. The structure is shown in Fig. IV.15. The configuration is a little complicated at first sight as the lattice is composed of layers each of which has three planes of oxygen atoms. Cations, either of aluminium or iron, are in distorted six-fold co-ordination within these layers. Half the oxygens of a layer touch four cations and thus receive their full valency share; the other half are in contact with only two cations but are linked to oxygens in other layers through two hydrogen atoms, thereby completing their valency requirements. Therefore it

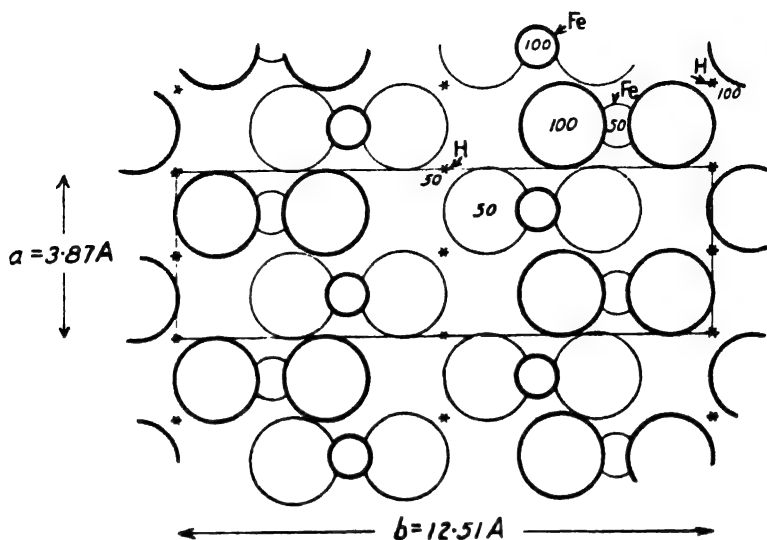


FIG. IV.15. THE STRUCTURE OF BOEHMITE AND LEPIDOCROCITE
(after Bragg)

is better to represent the formulæ of boehmite and lepidocrocite as $\text{RO}(\text{OH})$ whereas diaspor and goethite are more logically described as HRO_2 .

The constants of lepidocrocite are:

Lepidocrocite $\text{FeO}(\text{OH})$
Space Group: Amam
 $Z = 4$

System: Orthorhombic
Axes:
 $a = 3.87 \text{ \AA}$
 $b = 12.51 \text{ \AA}$
 $c = 3.06 \text{ \AA}$

Boehmite has the same structure but with $a = 2.85 \text{ \AA}$, $b = 12.2 \text{ \AA}$ and $c = 3.69 \text{ \AA}$.

HYDRATES

MANY compounds containing the elements of water are not definite chemical entities, but have the molecules of water attached very loosely to the structure. Water is lost at comparatively low temperatures without disruption of the compound and involves little rearrangement within the crystal itself. The term 'hydrates' is often used to distinguish compounds of this type from the *hydroxides* in which the water is held firmly as an integral part of the structure.

Some hydrate structures will be considered in the following pages.

CARBONATES

THE carbonates of the alkaline earth elements form a very important series of possible basic refractories. The mineral magnesite and the composite calcium-

magnesium carbonate, dolomite, are used as such but the others fail to form stable oxides and cannot, *as yet*, be used on an extensive scale.

The atomic structure of these carbonates is quite simple despite the fact that the complex unit or ion CO_3^{2-} is present. Bragg¹ has shown that the structure of *calcite* (calcium carbonate, CaCO_3) closely resembles that of *rock-salt*, NaCl , in which calcium ions replace sodium and the carbonate radicle takes the place of chlorine. But, because the carbonate radicle is non-symmetrical, it lowers the symmetry and destroys the cubic arrangement of the unit cell. Calcite is rhombohedral with constants of:

Calcite CaCO_3	System: Rhombohedral
Space Group: $R\bar{3}c$	Axis: $a = 6.361 \text{ \AA}$
$Z = 2$	Angle: $\alpha = 46^\circ 07'$

An interesting feature of the alkali carbonates is the change-over of structural type with an increasing ionic size of cation. Elements which have smaller ions than calcium form crystals similar to calcite itself, but those of larger sizes have a different configuration. Calcium carbonate has the distinction of being able to form both modifications, the first of which is rhombohedral *calcite*, which has already been mentioned, and the other is *aragonite* of orthorhombic symmetry.

The two series of minerals are compared in Table IV.VII, which also gives the ionic sizes of the cations and the lattice parameters.

TABLE IV—VII. LATTICE CONSTANTS OF THE
ALKALINE EARTH CARBONATES

	Mineral	Composition	Size of ion	Space group	Parameters	
					Axis	Angle
Calcite Group (rhombohedral)	Magnesite	MgCO_3	0.78 Å	$R\bar{3}c$	$a = 5.61 \text{ \AA}$	$\alpha = 48^\circ 10'$
	Siderite	FeCO_3	0.83	"	5.82	$47^\circ 45'$
	Smithsonite	ZnCO_3	0.83	"	5.62	$48^\circ 20'$
	Rhodochrosite	MnCO_3	0.91	"	5.84	$47^\circ 20'$
	Calcite	CaCO_3	1.06	"	6.36	$47^\circ 07'$
	Dolomite	$(\text{CaMg})\text{CO}_3$	—	$R\bar{3}$	6.00	$47^\circ 30'$
	Ankerite	$\text{Ca}(\text{Mg, Fe})(\text{CO}_3)_2$	—	—	—	—
Aragonite Group (orthorhombic)	Aragonite	CaCO_3	1.06	Pcmm	$a = 4.94 \text{ \AA}$	$b = 7.94 \text{ \AA}$
	Strontianite	SrCO_3	1.27	"	5.12	8.40
	Cerussite	PbCO_3	1.32	"	5.14	8.45
	Witherite	BaCO_3	1.43	"	6.25	8.83
	Bromilite	$(\text{Ca, Ba})\text{CO}_3$	—	—	—	—

The essential difference between the calcite and aragonite structures lies in the relative positions of the carbonate ion and the calcium ion. In both cases, the calcium ions are in hexagonal close-packing, but in the calcite group, each oxygen of the carboxyl group touches two cations, whereas in the aragonite group they are in

¹ Bragg, W. L., *Proc. Roy. Soc.*, **A89**, 468, 1914.

contact with three cations (see Fig. IV.16). The $(\text{CO}_3)^{2-}$ ion must therefore be placed asymmetrically in aragonite with respect to two layers of calcium ions.

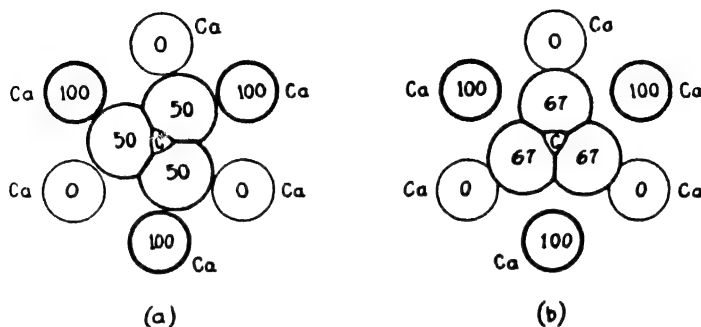


FIG. IV.16. THE STRUCTURES OF CALCIUM CARBONATES
(after Bragg)

(a) Calcite; and (b) aragonite

Dolomite is sometimes assumed to be:

- (a) a definite mineral, MgCaC_2O_6 ;
- (b) a form of calcite in which part of the calcium has been replaced by magnesium;
- (c) a mixture of calcium carbonate and magnesium carbonate.

X-ray examinations show that it is a single substance,¹ but of variable composition.

Some deposits known as *magnesian limestone* may be mixtures of calcium carbonate and magnesium carbonate and should not be described as 'dolomite'.

The *simple alkali carbonates* (soda, potash and lithium carbonate) are, ceramically, of interest mainly because of their occurrence as impurities in clays, etc., and their use as constituents of glaze-frits. Their atomic and crystal structure is of small importance in ceramics, and for that reason is not described in this volume.

SULPHATES

SULPHATES are also examples of complex ion configurations, and once again two types of structure are associated with the sulphates of the important group of divalent elements.

The elements with large cations form structures of the *barytes* type; those with small ions have the *anhydrite* structure; calcium sulphate can only have the latter structure.

Both barytes and anhydrite crystallise with orthorhombic symmetry, but their space groups are different. In *barytes*, BaSO_4 , a barium ion lies between twelve oxygens of sulphate radicles; in *anhydrite*, CaSO_4 , a calcium ion is linked to eight oxygens, not all of which are at the same distance from it.

¹ Bradley, A. L. and Jay, A. H., *Iron and Steel Inst. Sp. Rep.*, No. 33, 48, 1946.

The constants of minerals in the sulphate group are given in Table IV.VIII.

TABLE IV—VIII. LATTICE CONSTANTS OF THE ALKALINE EARTH SULPHATES

	Name	Chemical composition	Size of ion	Space group	Parameters		
					a	b	c
Anhydrite Group (orthorhombic)	Anhydrite	CaSO ₄	1.06 Å	Ccmm	6.22 Å	6.96 Å	6.97 Å
Barytes Group (orthorhombic)	Celestite	SrSO ₄	1.27	Pnma	8.36	5.36	6.84
	Anglesite	PbSO ₄	1.32	„	8.45	5.38	6.93
	Barytes	BaSO ₄	1.43	„	8.85	5.44	7.13

Gypsum, CaSO₄·2H₂O, is monoclinic in structure and like some hydroxides has a layer-lattice. Each layer contains sulphate radicles (SO₄)²⁻ linked to calcium ions as shown in Fig. IV.17. A calcium ion is surrounded by eight units, six of these are oxygen ions, of which there are two from each of three sulphate groups, and the other two co-ordinating groups are water molecules. The linking between layers is through these water molecules which have weak bonds and give rise to cleavage along these planes.

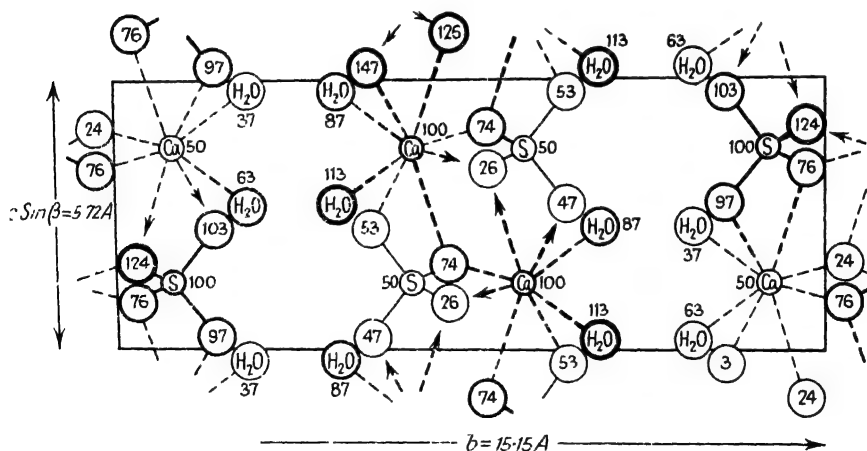


FIG. IV.17. THE STRUCTURE OF GYPSUM (after Bragg)

Plaster of Paris, 2CaSO₄·H₂O, has a structure akin to zeolites in that water may be removed without destroying the crystal lattice. Thus on heating to about 300° C. it forms *soluble anhydrite*, CaSO₄, which has the same structure and reacts in the same way with water. On heating to a higher temperature a further change in structure occurs and *normal anhydrite* is formed.

Alkali sulphates occur chiefly as adventitious impurities in clays and other ceramic materials. Their structure is of small importance to ceramists and is therefore omitted from this volume.

Alunite, $\text{KAl}_3(\text{OH})_6(\text{SO}_4)_2$. The mineral *alunite* is sometimes associated with clays. Its structure is rhombohedral with each aluminium atom surrounded by four OH groups and two oxygen atoms from sulphate ions. Potassium ions are in twelve-fold co-ordination with six oxygen atoms and six OH groups.

There are many minerals in the alunite group but only three need be mentioned; these are *alunite* itself, the iron isomorph, *jarosite*, $\text{KFe}_3(\text{OH})_6(\text{SO}_4)_2$, and the sodium analogue, *natro-alunite*, $\text{NaAl}_3(\text{OH})_6(\text{SO}_4)_2$.

The structural constants of alunite¹ are:

Alunite $\text{KAl}_3(\text{OH})_6(\text{SO}_4)_2$
Space Group: R3m
Z = 1

System: Rhombohedral
Axis: $a = 7.05 \text{ \AA}$
Angle: $\alpha = 59^\circ 02'$

OTHER OXYGEN SALTS

Phosphate minerals, particularly *apatite*, occur in some clays and so do *coprolites* and *phosphorite* produced from organic remains, but these are only 'impurities' and their structure is of little importance. The most important phosphate used in chinaware is *bone ash*, made by calcining bones. Little is known of its structure but it appears to resemble that of silicates, the PO_4 -ions in bone ash occupying the same positions as the SiO_4 -ions in calcium silicates.

In a PO_4 tetrahedron, three oxygen atoms form normal valencies and each possesses a free valency whilst the fourth is inactive. The P—O—P bond angle is fixed at about 126° but sufficient ionic character is retained for this angle to be variable and to enable glasses to be formed. As the PO_4 tetrahedron has only three linkages a phosphate glass has a low softening point.

Other groups which occur in minerals include phosphates, tungstates, borates, etc. Many of these have not been investigated fully and others are beyond the scope of this volume. An interesting feature of some borates is that they have a framework structure based on boron and are comparable with the silicates (see also p. 187).

SULPHIDES

THE sulphides are a highly complex group of minerals because of the high degree of polarity of the sulphur atoms. There are many important sulphide groups, but only the few of interest to ceramists will be mentioned in this volume.

Iron sulphides are known to exist in many forms. *Pyrrhotite*, FeS , is often called magnetic pyrites and is occasionally associated with Cornwall granite. The structure is based on a hexagonal unit cell and there is usually an excess of sulphur on analysis.

Pyrite,² FeS_2 , is the most commonly occurring form of iron sulphide. Its

¹ Gossner, B., *Zett. Krist.*, 96A, 488, 1937.

² The term *pyrites* is a general one for all iron sulphides, and its use for *pyrite*, FeS_2 , is incorrect, but frequent. The letter *s* should be omitted when pure, crystalline pyrite is intended.

crystal structure may be compared to that of rock-salt, NaCl, in which the sodium ion is replaced by iron and the chlorine ion by a dumb-bell group of two sulphur atoms. The structure is illustrated in Fig. IV.18, and the constants are:

Pyrite FeS_2
 Space Group: $\text{Pa}\bar{3}$
 $Z = 4$

System: Cubic
 Axis: $a = 5.40 \text{ \AA}$

The sulphur to sulphur distance is only about 2.10 \AA , thereby suggesting that a considerable amount of covalent linking is present.

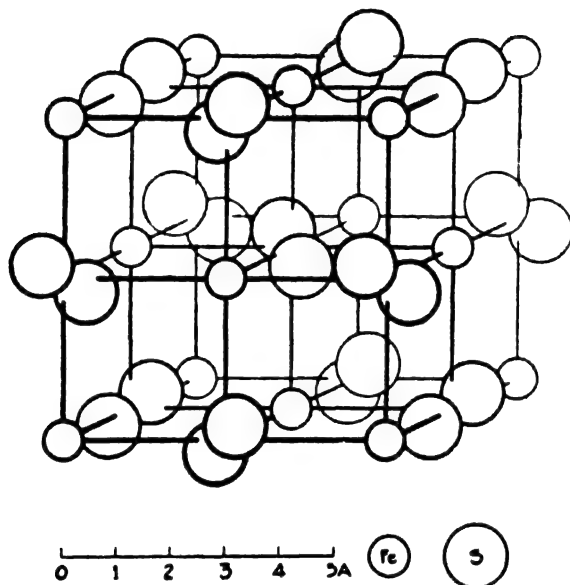


FIG. IV.18. THE STRUCTURE OF PYRITE
 (after Bragg)

Marcasite, FeS_2 , has a rather similar configuration to pyrite, but the unit cell is orthorhombic with constants of:

Marcasite FeS_2
 Space Group: Pmnn
 $Z = 2$

System: Orthorhombic
 Axes:
 $a = 3.37 \text{ \AA}$
 $b = 4.44 \text{ \AA}$
 $c = 5.39 \text{ \AA}$

Chalcopyrite, CuFeS_2 , is the well-known copper pyrites. Its structure is based on that of *zinc-blende*, ZnS , which crystallises in the tetragonal system. Each sulphur atom lies between two copper and two iron atoms which are situated at the corners of a tetrahedron. The structure is shown in Fig. IV.19, and the constants are:

Chalcopyrite CuFeS_2
 Space Group: $I42d$
 $Z = 4$

System: Tetragonal

Axes:
 $a = 5.24 \text{ \AA}$
 $c = 10.30 \text{ \AA}$

The unit cell of chalcopyrite is twice as large as that of zinc-blende and corresponds to two cubes one above another.

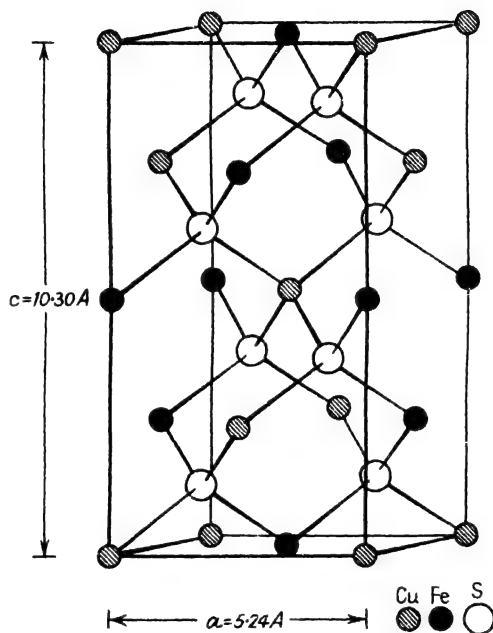


FIG. IV.19. THE STRUCTURE OF CHALCOPYRITE
 (after Pauling and Brockway)

Dark-shaded circles, iron atoms; light-shaded circles, copper atoms; open circles, sulphur atoms

Embscrite, CuFeS_2 , is a variety of chalcopyrite found in some clays.

Galena, PbS_2 , is chiefly of interest as one of the main sources of lead and the lead oxides. It has a cubic structure like rock-salt but with six equidistant sulphur atoms at 2.97 \AA .

CARBIDES

CARBIDES do not occur in nature in commercially useful quantities. Those used industrially are all manufactured and are usually known by trade names.¹ Those of ceramic interest are *silicon carbide* and *tungsten carbide*. These commercial products are not usually very pure crystals; some of them vary considerably from

¹ *Carborundum* is the registered trade mark of carbides manufactured by the Carborundum Co. and should not be applied to carbides made by other firms though this is often done.

the 'ideal' formula, M_xC_y , and probably consist of mixtures of carbides, carboxides and unaltered raw materials.

Silicon carbide, SiC. The crystal structure of silicon carbide was first determined in 1944 by Thibault,¹ who found that among a profusion of types, there are two main modifications—an α -form with a hexagonal structure and a β - or cubic variety. The former, which predominates in commercial abrasive powders, may be subdivided into at least five different forms, all of which have characteristic structures and space groups.

Tungsten carbide, WC, crystallises in the cubic system, but appears to exist as more than one modification.

OTHER NON-SILICA MINERALS

THERE are many more non-silica materials of importance in ceramic studies, but it is impossible to catalogue them here. New developments in ceramics include those of particular interest in applications of nuclear and atomic energy and a new field in high-temperature refractories will probably develop as a result of experiments along these lines.

¹ Thibault, N. W., *Amer. Min.*, 29, 249, 327, 1944.

CHAPTER V

THE IDENTIFICATION AND ESTIMATION OF MINERALS IN CERAMIC MATERIALS

MANY of the properties of clays and other ceramic materials are dependent on the nature and amounts of the various minerals in them, so that their identification, determination and estimation¹ are of very great importance. The problem is made more difficult because ceramic materials are rarely composed of one pure crystal type. Usually, several minerals are present in appreciable quantity, and many others as minor constituents; whilst the identification of a particular pure mineral may be comparatively easy, there is usually much more difficulty when others are present especially if they are of similar type.

In some cases, one mineral cannot be differentiated from others with which it is associated unless there is some prior purification. This is particularly true of many clays, and details of a useful method for separating the minerals from such materials are given later in this chapter. Clays are very diverse in composition and some contain many mineral types. In addition to the clay minerals (see Chapter III), quartz, micas and other components may be present in considerable amounts.

Furthermore, many ceramic materials are of small grain size. This is again exemplified by clays where particles as small as 100 Å (i.e. 10^{-6} cm.) are of frequent occurrence. The identification of such minerals is extremely difficult for they are too small to be observed except with an electron microscope.

The mineralogist is also faced with the difficult problem of isomorphous substitution, for many minerals vary within wide limits of chemical composition. In many instances different grains of a particular mineral may show pronounced differences in property and composition; this is particularly true of micaceous flakes in sedimentary deposits.

Therefore, in general, methods of analysis must be capable of detecting and estimating minerals which may not be of constant composition, which are usually admixed with other types and sometimes of very small grain size.

The identification of a mineral must depend on some fundamental characteristic which is always the same, independent of the mode of occurrence or the nature of the locality or environment. Methods of mineral identification have been devised which make use of a particular property or class of properties. They can be summarised as:

¹ A *determination* is the result of definitely ascertaining the position, nature, amount, etc., of anything by measurement, weighing or counting.

An *estimation* is the result of approximately ascertaining numbers, quantities, magnitudes, etc., without actual enumeration, weighing or measurement or by using such limited means as are insufficient or unsuitable for producing an accurate and reliable result. For many purposes an estimation is sufficiently accurate but from its nature it cannot (except by coincidence) be as positive as a determination. This distinction is important but is not always realised.

1. Those dependent on the chemical nature of the mineral.
2. Those dependent on the external crystallographic features of the mineral, i.e. the microscopic properties.
3. Those dependent on the internal atomic or ionic arrangements within the crystal lattice; this group includes X-ray, infra-red and electron diffraction analysis.
4. Those dependent on some physical or chemical change within a mineral which can be measured under controlled conditions, such as differential thermal analysis (i.e. the measurement of heat changes which occur during reactions).

Other methods are known and used to identify and even roughly estimate minerals present in ceramic materials. Most of these use an inferred property of a mineral, and provided that only one mineral in a mixture exhibits this property the method can be of value. The magnetic properties of a substance may sometimes be indicative of the presence of iron-bearing minerals. The cation exchange capacity (see p. 264) may differentiate between montmorillonite and kaolin-containing clays. Properties such as plasticity, thixotropy, etc., also are of value in some cases in suggesting the presence or otherwise of certain minerals.

Sampling. The identification of minerals in a ceramic material does not usually require great care in the selection of samples. However, when it is necessary to ascertain the proportion of any mineral present, it is essential to procure one or more samples of ample size which are truly representative of the whole. If the total quantity of the material is large, it is highly important that any sample shall be typical of the whole and not of one (possibly abnormal) portion. Unless very great care is taken in obtaining a 'fair sample' the results of testing may be seriously in error.

A single piece, selected haphazardly from the mass, will be unlikely to be fairly representative, and even a large number of such casually selected samples may not be satisfactory. Very frequently large variations occur, so that it is most important that proper care should be taken to obtain a truly representative sample. When a large, natural deposit of clay or other material is to be analysed, the samples should be taken from many different parts of the bed, both horizontally and vertically. It is often desirable to have several distinct selections from different parts of the deposit, so as to determine whether the material is constant in composition throughout the whole bed. Where the material appears to be fairly uniform, about 1 per cent of the whole of the material may suffice for the preliminary sample from which the final is to be taken, but with a very heterogeneous material, 2 per cent or even 5 per cent may be necessary to obtain a reasonably typical sample. The preliminary sample should be composed of numerous smaller ones selected systematically from every part of the deposit and not merely from those which are the most readily accessible.

If the material to be examined is contained in trucks or in a heap, it is equally necessary to take an ample quantity in the form of small samples from many parts. Samples from large quantities of material contained in trucks or shiploads are often taken by means of mechanical appliances.

The preliminary sample is next treated as an original material from which a representative sample is to be obtained by the process known as 'quartering', which is usually effected as follows:

The material should be thoroughly mixed and placed in a symmetrical and

rather flat pile and divided into four equal parts. One of these parts is removed, the material in it is again mixed and then quartered, this being continued until a sample weighing about 28 lb. is obtained. This is coarsely crushed and again quartered, one quarter (about 7 lb.) being sent to the analyst, who should then obtain a representative sample by still further crushing and quartering until a suitable quantity is obtained. When very small samples are required for analysis, fine grinding and thorough mixing are very essential.

The samples sent to the analyst should not be ground too finely before transit, otherwise some compounds may be oxidised and so render the results inaccurate; thus, ferrous oxide may be oxidised into ferric oxide, and pyrite (FeS_2) to iron sulphate or oxide. Grinding is also undesirable because some minerals, especially those of platy character, may be destroyed. Phosphor-bronze instruments should be used as far as possible instead of iron or steel ones in sampling, grinding and sifting, so as not to include any adventitious iron in the sample. Other useful information relating particularly to the sampling of clays is to be found in a publication of the British Standards Institution No. 1902 (1952).

CHEMICAL METHODS

THE chief purpose of a full chemical analysis is to reveal all the elements present in a sample and the proportion of each. In some instances it may reveal the presence of an unsuspected mineral which might, otherwise, be overlooked.

The results of a chemical analysis of any substance are usually expressed in terms of the various oxides present, such as silica, alumina, titanium oxide, ferric and ferrous oxides, lime, magnesia, soda, potash, carbon dioxide, sulphur dioxide, water, etc. Such an analysis does not indicate the forms in which the various elements are combined and, when sulphides are present, the reporting of the results in terms of oxides introduces errors (usually small, but sometimes important) for which allowance must be made.

Prior to commencing a chemical analysis, the sample should be dried and ground as finely as possible—usually in an agate mortar, which does not add any appreciable amount of silica to the sample. Insufficient grinding may cause serious errors, especially when the substance is slow to react.

Many silicates and other naturally-occurring minerals are not readily attacked or broken down by common laboratory agents. The first step, therefore, in chemical analysis is to convert the mineral entities into a form in which the individual elements or oxides can be easily separated from each other. The following four methods are in fairly common use:

(a) The silica may be evaporated by heating with hydrofluoric and sulphuric acids in a platinum dish; the residue of sulphates or fluorides of the other elements, which are mostly readily soluble, may then be analysed. For many purposes, this removal of the chief constituent (silica) is particularly convenient. Some minerals are slow to react under this treatment, particularly those which have been produced at high temperatures (e.g. mullite). For this reason it is advisable to repeat the evaporation until a constant weight of residue is produced.

(b) The sample may be boiled with sulphuric acid; this decomposes it and leaves the silica in a free state so that (after baking) the other compounds present may be removed by solution in hydrochloric acid. The silica may then be separated by filtration and the other ingredients estimated in the customary manner. This method—long known as 'Rational Analysis' (a term proposed by Seger)—has limited application, because some materials are not completely decomposed and some decomposition products are not readily removed from the residue (e.g. calcium sulphate). Notwithstanding these objections, the method is often convenient where its limitations are appreciated, e.g. for works control and for investigations where the results are used in conjunction with other evidence.

(c) The sample may be heated to about 750° C. until it ceases to lose weight; this decomposes some minerals into component oxides with the evolution of water, carbon dioxide or other gas. The silica can then be extracted by solution in caustic soda and the alumina and iron compounds by solution in hydrochloric acid. Great caution is required in the interpretation of the results of this method, but it is less troublesome than the former treatments and for this reason it is in fairly common use. Many minerals, e.g. quartz, feldspar, micas, are not attacked under these conditions and remain as an insoluble residue. It is important to avoid a higher temperature of ignition than 750° C. otherwise the oxide components are rendered insoluble.

(d) The sample may be fused with molten sodium carbonate, sodium hydroxide or, for some purposes, with a mixture of calcium carbonate and ammonium chloride. Virtually all minerals are decomposed by this treatment and dissolve in the molten mass. Soluble carbonate salts of the non-acidic oxide components are dissolved in hot water and filtered from the insoluble carbonates, such as barium and calcium. When treated with dilute hydrochloric acid, the soluble carbonates in the filtrate are converted to chlorides and silica precipitated from sodium silicate.

Whichever method is used to decompose the original sample, the usual procedure of analysis is to precipitate, gravimetrically, compounds of the elements present. Use is made of the different solubilities of salts under certain conditions; thus silica is insoluble in hydrochloric acid whereas chlorides of aluminium, iron, calcium, etc., are completely soluble; hydroxides of aluminium, iron, chromium and titanium may be precipitated in a weak alkaline solution provided that the chloride ion concentration is high, yet under these same conditions, calcium, magnesium and the alkalis remain in solution. These latter elements may be separated by utilising the different solubilities of their oxalates and phosphates.

The alkali elements, sodium and potassium, form very few insoluble salts and consequently are difficult to estimate gravimetrically. Probably the best method is to use a flame spectrometer (see p. 216), although reliable chemical techniques have been developed. It is important to estimate each alkali element separately than to assess one by difference.

In recent years there have been attempts to reduce the tedium of the full silicate analysis and to shorten the time involved. Such methods utilise volumetric and colorimetric analysis for many of the components. Bennett¹ has given a summary of many of these techniques.

¹ Bennett, H., *Trans. Brit. Ceram. Soc.*, **54**, 319, 1955.

Space does not permit a detailed description of the methods employed in the ultimate chemical analysis of ceramic materials, and the reader who desires this information should refer to other volumes dealing more particularly with the subject, especially *Silicate Analysis* by A. W. Groves (Allen & Unwin, 2nd edition, 1951).

Chemical analysis as a means of mineral identification and estimation will obviously be of the greatest value when one particular mineral predominates in the sample, for if that mineral has a simple formula, it can be accurately assessed and the nature and amounts of the minor, accessory minerals may also be indicated. However, if a mixture of minerals is analysed, the result will give the total of each element or oxide, but no information about the nature and type of the actual minerals containing those elements. So, in a typical clay containing quartz, clay minerals, mica, etc., the total silica content on analysis will come in part from each silicate mineral present and the actual contribution of each cannot be determined. Taken by itself, therefore, a chemical analysis of a composite rock, mineral deposit or fired product is of little value in the estimation and detection of the minerals present, but when used in conjunction with other methods of analysis, it can be of very great importance.

To a ceramist who is not specifically concerned with the derivation of mineralogical composition, a chemical analysis is often very useful. For example, the alumina/silica ratio of a clay may indicate the approximate value of that material as a refractory. Similarly, the total content of alkalis in a clay will show whether the material is likely to have a high melting point, but it would not be safe to predict the vitrification temperature on this result alone. Soda and potash, when in the form of feldspar, are more detrimental to the refractoriness of a clay than when they are in the form of mica, because the former melts more readily. Sodium silicate is still more easily fusible.

A chemical analysis is also valuable in showing the presence of some deleterious ingredients, such as (i) lime, which may destroy bricks and tiles made of clay containing it, or (ii) ferric oxide, which may either discolour or enhance the beauty of the product, depending on whether a white or red material is desired, or (iii) alumina, which in siliceous refractories greatly reduces the load-bearing capacities at high temperatures.

A complete analysis, including those elements which are present in very small proportions (less than 0.1 per cent), is very rarely required but the possible need for it should never be ignored, as the omission of a small percentage of some constituents may make adequate interpretation of the results of the analysis very difficult. For this reason, no constituents should be estimated 'by difference' in order to make the analysis complete, though this is frequently done. It is especially important that the alkalis should not be 'estimated' in this way, as a small error in the proportion of them may have a serious effect in the interpretation of some of the properties of the material. Duplicate determinations should always be made and, if careful and accurate procedures are adopted, they should not differ by more than 0.1 per cent.

Selective Chemical Analysis. The separation of one or more minerals from others in a mixture by a chemical agent is, where practical, of great importance. Such separation may be achieved in either of two ways: (i) where a single mineral entity is attacked by a specific reagent and converted into a form in which it can be extracted

from the other components, and (ii) where all the ingredients of a composite material are destroyed except one, which can then be estimated.

Probably the best example of the first method is the estimation of carbonates in rocks by measuring the carbon dioxide evolved on treatment with dilute hydrochloric acid. The type of carbonate may then be determined by analysing the cations passing into the acid solution. Also of value are the methods of estimating free oxides of iron and sometimes aluminium in clays. These minerals are present in many cases, not as discrete particles, but as a colloidal film surrounding grains of other minerals and may be troublesome if a complete mineral balance is required. The method of Dion¹ has been used with considerable success, where, under carefully controlled conditions, goethite can be quantitatively removed from clays. Iron oxide dissolves in a weak alkaline solution in the presence of nascent hydrogen, conditions which are secured by treating the clay with a boiling solution of ammonium tartrate in an aluminium or porcelain vessel. The rate of reaction is accelerated by the addition of spirals of aluminium which should be freshly cut from sheet metal at the start of the experiment.

Hallimond² has outlined a method for the preferential solution of chlorites in dilute acid solutions, but the raw material must be free from other acid soluble components.

A chemical method³ has been described which is claimed to be capable of distinguishing between four-fold and six-fold co-ordinated aluminium in layer structures.

The chemical estimations of quartz or free silica involve destroying all other minerals by violent acidic reagents, which have little or no effect on the silica component. Trostel and Wynne⁴ favour the use of fused potassium bisulphate, whereas Shaw and Skinner⁵ prefer to use a mixture of sulphuric and hydrochloric acids. In both methods, any silicates that may be present are decomposed, thereby leaving some colloidal silica in suspension, which can be removed by careful treatment with sodium hydroxide.

These methods attempt a compromise because too violent a treatment unquestionably results in the solution of some free silica; on the other hand, some silicates—e.g. feldspar and mullite—require prolonged treatment before they are completely decomposed. Correction factors have recently been proposed to allow for the errors that are introduced.

SPECTROGRAPHIC ANALYSIS

SPECTROGRAPHIC analysis may be regarded as an adjunct to chemical methods, for this also enables the individual elements to be identified and in some cases estimated.

It is based on the fact that at very high temperatures, such as those attained in an electric arc or a suitably produced series of sparks from an induction coil, the movement of electrons in their orbits is disturbed and characteristic radiation emitted.

¹ Dion, H. G., *Soil Sci.*, **58**, 41, 1944.

² Hallimond, A. F., *Spec. Rep. Min. Res. Mem. Geol. Survey Gt. Britain*, vol. 29.

³ Brindley, G. W. and Youell, F., *Acta Cryst.*, **4**, 495, 1951.

⁴ Trostel, L. J. and Wynne, D. J., *J. Amer. Ceram. Soc.*, **23**, 18, 1940.

⁵ See Nagelschmidt, G., *The Analyst*, **81**, 210, 1956 (Appendix).

Thus, if a sample of the powder to be analysed is placed between carbon rods and a high-frequency current is applied, the radiation emitted by these electrical disturbances within the atoms can be projected through a prism on to a photographic plate. As the radiation from each element is of a characteristic wavelength, a series of lines is produced on the plate, each of which is a result of an electronic change in the particular element. These lines may be calibrated and the elemental composition of any particular powder determined. The amount of a particular element may often be estimated, as it is proportional to the intensity of its characteristic line or lines in the spectrographic pattern, provided that the test has been carried out under standard conditions. The method is rapid and is of especial value in the identification and estimation of elements present in small amounts. The line-pattern produced by a single element may contain a profusion of lines; hence, if many elements are present, the resulting pattern is complicated and difficult to analyse. Increasing use is being made of spectrographic methods, and their value as a means of estimating alumina associated with silica in raw quartzites and in fired bricks has been demonstrated by Mason and Speight.¹ A comprehensive survey of spectrochemical methods and their application in the analysis of silicates has been published by Ahrens.²

FLAME PHOTOMETRY

MOST students of chemistry are aware that sodium compounds when introduced into a flame, colour it yellow, and the violet and brick-red colorations of potassium and calcium respectively are equally well known. These characteristic emissions are again the result of disturbances in the electron orbits of the elements, but where the wavelength of the emission is in the visible region of the spectrum.

Within the last few years, the development of commercial flame photometers has greatly relieved the tedium of many of the processes in silicate analysis and, at the same time, increased the accuracy with which many elements can be estimated. The essential features of the instruments are a suitable flame and a means of ejecting a solution of the sample into it at a predetermined rate. A filter, designed to transmit only the characteristic emission of a particular element, is placed between the source and a photocell so that the intensity of radiation may be measured and compared with standard samples tested under the same conditions.

The content of calcium, potassium and sodium in a material can be rapidly and accurately assessed in most spectrometers and others can be adapted to estimate lithium, barium and other elements.

CHROMATOGRAPHIC ANALYSIS

THIS method of analysis involves the use of a comparatively new technique, but which is likely in the coming years to supersede many of the conventional analytical procedures.³ Chromatographic analysis depends on the fact that when different substances are absorbed, suspended or dissolved in a medium, they travel through

¹ Mason, G. L. and Speight, G. E., *Trans. Brit. Ceram. Soc.*, **50**, 35, 1951.

² Ahrens, L. H., *Quantitative Spectrochemical Analysis of Silicates* (Pergamon, 1955).

³ Williams, T. L., *The Elements of Chromatography* (Blackwell Ltd., Oxford, 1954).

that medium at different rates, so that a separation of them is effected. The method has been used to a considerable extent in gas analysis, but it is equally effective in the estimation of mixed solutions. The usual technique is to allow the solution to run slowly down an inclined paper impregnated with a suitable resin; after a certain period of time, the components of the solution will have reached different levels on the paper, where they can be estimated, usually by colorimetric techniques.

Recalculated Analysis. Although the methods of analysis so far described indicate only the type and amounts of elements present in a sample, it is sometimes convenient to recalculate the results to give an indication of the mineralogical composition. At the best, only an approximate mineral balance will be given, and where the material is complex, containing several components, so many assumptions have to be made that the recalculation may be of little value. In samples where the major mineral entities are known or can be identified by other means, recalculation of the chemical analysis can be most informative. Fireclays, for example, contain predominantly three mineral entities, quartz, mica and the kaolin clay mineral, livesite; the total alkali content will be present as mica (apart from a small proportion of exchangeable cations associated with the clay mineral) so that the proportion of this mineral can be assessed; the alumina content comes from both mica and livesite, but knowing the content of the former, the latter can be calculated; the remaining silica, after subtracting that present in the mica and livesite, will be as quartz or some other form of free silica. Recalculated analysis used in this way can give a mineralogical balance which is in close agreement with that obtained when each mineral is assessed separately by other methods. It can be extremely misleading, however, if a major component is overlooked.

MICROSCOPIC EXAMINATION AND ANALYSIS¹

THE observation of the external form of minerals either by eye or under magnification has been one of the principal methods of identification and analysis from the earliest days of mineralogy. It was recognised that particular mineral species always formed crystals of exactly the same type and shape, and with definite characteristics whereby they could be differentiated from others. The use of the *polarising* microscope establishes not only the external crystal form but also many other important optical properties of minerals.

A microscope is also invaluable for observing many other facts about ceramic materials (both raw and manufactured) in either their natural, polished or powdered state. It may be used to study defects in ceramic bodies and to investigate the texture of both raw materials and manufactured products.

For many purposes, a hand-magnifier is sufficient, for others a low-power microscope magnifying 20–50 diameters, but for an exhaustive examination a good, modern, petrological microscope with a magnification of up to one thousand times is needed. Useful accessories to such an instrument include a universal stage,

¹ The microscopical examination of minerals has been described in great detail by numerous authors. The reader is recommended to consult (i) Winchell, A. N., *Elements of Optical Mineralogy* (Chapman & Hall, London, 1947); (ii) Rigby, G. R., *The Thin-section Mineralogy of Ceramic Materials* (British Ceramic Research Association Pub., Stoke, 1953).

It may be used as a means of high magnification, the magnitude of which is governed by the selected combination of *objective* (O) and *eyepiece* (E) lenses. The *mirror* (M), situated below the *stage* (S) of the microscope, is usually flat on one side and concave on the other, so that a beam of either parallel or convergent light may be projected upwards through the section and instrument; in examinations in ordinary light the flat side is invariably used so that a parallel beam of light is employed.

Two nicol prisms or other polarising media are provided on all petrological microscopes—one below the stage, which is called the *polariser* (P), and another above the objective, which is termed the *analyser* (A). If the lower one only is inserted in the beam of light then the emerging rays vibrate in only one direction or plane, and the section can thus be examined in *plane polarised light*. If, however, both the polariser and the analyser are placed in position, the light is completely *polarised* provided that the nicol prisms are in the 'crossed' positions, where the vibration direction of one is at right angles to that of the other.

Alternatively, the section can be examined in convergent light in conjunction with crossed nicols when *interference figures* are produced. These can be seen quite clearly either by using the subsidiary *Bertrand lens* (B), or by removing the eyepiece (E). Useful information may be derived from an examination under all these four conditions.

(a) **Under Ordinary Light.** The first examination is best made using a low-power magnification. The composition of the section as a whole will then be revealed; many different mineral species may be observed, some of which may be transparent, others opaque and occasionally some may be coloured. The particle size of each mineral may be compared, and if the eyepiece is fitted with a calibrated scale then the actual size of each crystal can be measured.

The texture and general appearance of the section may indicate whether the material is of igneous or sedimentary character.

After the preliminary investigation has been completed, high-power magnification ($\frac{1}{4}$ in., $\frac{1}{8}$ in. and $\frac{1}{16}$ in. objectives in turn) may be used to study each different mineralogical variety in more detail. Sometimes the *crystal habit* or form of a mineral may be revealed in a well-developed fragment; in other cases, the angles between adjacent sides or faces can be measured using the rotating, calibrated stage of the microscope to bring first one side and then the other parallel to the cross-wires in the eyepiece. Care must be taken in such measurements, as the angle between faces is dependent on the inclination of the crystal with respect to the flat face of the section.

In most cases, the minerals present in a rock slice will be imperfect and the external characteristics will offer little indication of the crystal form or habit, but some minerals show pronounced *cleavage*, or a tendency to fracture along definite planes. Mica is an example of a mineral with perfect cleavage parallel to the basal section, for, as shown in Chapter III, it is composed of layers or plates, each held together by weak bonds, and it is along such planes that cleavage will develop. Other minerals may show more than one set of cleavage lines. The angle between these planes may be diagnostic of that particular mineral.

One of the most useful determinations which is carried out in ordinary light

is the measurement of the *Refractive Index*¹ of the mineral. Briefly, the refractive index of a material is defined as the ratio between the velocity of light in that material and its velocity in air.

The refractive index is characteristic for a particular mineral although its value may vary when measured along different optical directions within the crystal.

The measurement of refractive index is by far the simplest and most direct method of distinguishing between some transparent substances—particularly when they have the same composition but different physical properties, such as quartz, cristobalite, and tridymite, calcite and aragonite, lightly-calcined magnesia and periclase. It is an important means of ascertaining the proportion of unaltered quartz in silica bricks.

The *Becke method* is the most usual way of determining the refractive index of a mineral. A sample of the crushed mineral or rock is immersed in a liquid of known refractive index on a microscope slide. The barrel of the microscope is adjusted until the fragments are in focus and it is then raised slowly. A halo of light either surrounds or is enclosed by the particles when they are slightly out of focus, and this either expands or contracts as the barrel is raised further. The general rule is that when the microscope barrel is raised, the light halo moves from the medium of higher refractive index to the medium of lower index. Thus, if the immersion liquid is of lower refractive index than the mineral, the light halo will move outwards from the fragments, and the opposite will occur when liquids of greater refractive index are used.

When the index of the immersion liquid is similar to that of the mineral under examination the haloes are replaced by coloured bands, and if the fragments are transparent and colourless, they will be almost indistinguishable against the background. Provided that a range of liquids with slight variations in refractive index is available, accurate determinations can be made. An alternative method is to mix a liquid with a higher refractive index than the specimen with a liquid of lower index until the correct value is reached. The refractive index of the mixed liquids, and hence that of the specimen, can then be measured by means of a refractometer.

If a specimen, consisting of two minerals of different refractive index, is immersed in a liquid with the same index as one of them, that mineral will be almost or quite invisible, but the other will be clearly observed under the microscope. This method devised by A. B. Dick is a very delicate one and has been used for many years to distinguish tridymite from cristobalite in silica bricks. The solution used is mercuric-potassium iodide which has a refractive index of 1.477, the same as that of tridymite, whilst that of cristobalite 1.484.

A useful set of liquids of value in the determination of refractive indices is given in Table V.I.

Care should be taken, when using mixtures of liquids, that the components are miscible and have a similar vapour pressure. Suitable combinations which cover the range of refractive indices normally required in mineral studies are as follows:

¹ For the general theory of the refractive index of minerals the reader is referred to the standard textbooks on mineralogy, petrology and optics.

Care must be taken to avoid confusing the term refractive (which relates to the behaviour of light) and *refractory* (which is the capacity of a substance to withstand heat).

1.330-1.362	Methyl alcohol and ethyl alcohol
1.362-1.445	Ethyl alcohol and ethylene dichloride
1.445-1.538	Ethylene dichloride and ethylene dibromide
1.538-1.598	Ethylene dibromide and bromoform
1.598-1.658	Bromoform and α -bromo-naphthalene
1.658-1.727	α -bromo-naphthalene and methylene iodide
1.727-1.84	Methylene iodide and various sulphides and sulphur

Once proficiency has been acquired in measuring refractive indices, values can be determined rapidly and with great accuracy. In addition, a composite mixture may be analysed without prior separation of the components, and the refractive indices parallel to different crystallographic directions in a mineral can be assessed.

TABLE V-1. REFRACTIVE INDICES OF SOME IMMERSION LIQUIDS

<i>Material</i>	<i>Refractive Index</i>	<i>Material</i>	<i>Refractive Index</i>
Methyl alcohol	1.330	Ethyl salicylate	1.523
Ethyl alcohol	1.362	Ethylene dibromide	1.538
Ethyl acetate	1.373	Nitro-benzene	1.552
Amyl acetate	1.396	Benzyl benzoate	1.569
Ethyl bromide	1.424	Bromoform	1.598
Ethylene dichloride	1.445	Iodo-benzene	1.619
Liquid paraffin	1.470	Quinoline	1.625
Xylene	1.490	α -Bromo-naphthalene	1.658
Benzene	1.500	Methylene iodide	1.727

Among other useful information which may be revealed by examination in ordinary light is the *degree of alteration* and the *inclusions* within a particular mineral. Felspars are frequently changed by weathering action to clay minerals, and traces of the alteration product may be visible under the microscope. Quartz crystals often contain occluded fragments of other minerals and, more particularly, liquid or gas bubbles.

(b) In **plane-polarised light** some materials show a colour change as they are rotated upon the stage of the microscope. This phenomenon is termed *pleochroism* and is well illustrated by the micaceous mineral, biotite, which exhibits a colour change from a pale to a dark brown.

Some other minerals, which are colourless, exhibit twinkling or rapid changes of relief as the section is rotated on the stage.

(c) **Between crossed nicols or under polarised light**, minerals fall into one of two classes, (i) *isotropic*, or (ii) *anisotropic*. If a mineral fragment is examined under these conditions and it remains dark during a complete rotation of the section, it is said to be *isotropic*. If, however, the mineral is alternately dark and illuminated as the stage rotates, it is *anisotropic*. Cubic crystals and certain sections of other crystals are isotropic, all others are anisotropic. Minerals of the latter group show darkness (extinction) and illumination four times in succession during a complete

rotation of 360° of the stage. If the angle at which the extinction occurs can be referred to a principal crystallographic direction in the mineral, then the *extinction angle* can be measured.

At maximum illumination, a fragment may be white or coloured, depending on the optical orientation of the mineral, its birefringence (see below) and the thickness of the section. The plane-polarised light passing through the sub-stage polariser is resolved into two vibration directions at right angles to each other within the fragments of minerals in the section. In anisotropic crystals, light travels at different velocities along the main crystallographic directions, and therefore, the refractive index is different along each of these axes. If light entering the section is resolved into two components vibrating along two directions at right angles, it follows that one of these beams will be retarded relative to the other. If a certain mineral is oriented along one of its crystallographic axes, the amount of retardation will be directly proportional to the difference in the refractive index along this direction and that at right angles to it. The retardation is characterised by the development, at maximum illumination, of a specific spectrum colour of one of seven orders, and the Newton Colour Scale has been drawn up enabling the retardation to be calculated directly. The difference in the refractive indices in two major crystallographic directions is termed the *birefringence* and is often used in the identification of minerals. It may be calculated from the retardation and the thickness of the section by graphical means. (For further details the reader should refer to the books recommended on p. 217.)

The examination of sections under crossed nicols is of great value, for anisotropic minerals are thrown into relief, especially if they are contained in an isotropic, glassy matrix. In addition, if more than one mineral is present in a section, they may often be distinguished by the differences in birefringence. This is strikingly illustrated by the silica minerals quartz, cristobalite and tridymite. The first is often present as small mineral fragments agglomerated together, as in quartzites, where its comparatively high birefringence bestows a characteristic coloured mosaic when a section is examined under polarised light. Cristobalite and tridymite (which are present in silica bricks) are clearly distinguished between crossed nicols, the former because of the weak anisotropic nature of its small, globular crystals, and the latter by its characteristic twinned arrow-heads. Photomicrographs of these three minerals under polarised light are shown in Fig. V.2a, b, and c, facing p. 224.

Other alumino-silicate refractories show characteristic features in thin sections which can be distinguished under the microscope. Siliceous fireclays usually contain a high proportion of unchanged quartz, which is readily recognised in polarised light (Fig. V.2d). Less siliceous fireclays appear amorphous or glassy, although occasionally finely-divided mullite can be observed (Fig. V.2e). As shown in Fig. V.2f, mullite is the predominant mineral in aluminous fireclays (circa 72% Al_2O_3); this mineral has an unmistakable needle-like structure clearly revealed in polarised light. Sillimanite refractories, manufactured from calcined kyanite, are also rich in mullite and, as Fig. V.2g shows, the original grains of kyanite can be observed, criss-crossed with mullite. Corundum, $\alpha\text{-Al}_2\text{O}_3$, is the predominant mineral in alumina refractories; it is present as angular fragments of high relief (Fig. V.2h).

Many minerals, some of which are commonly associated with ceramic materials, exhibit *twinning*, i.e. crystals exist in which one part is aligned at a different crystallographic direction from another. When such a crystal is observed under the microscope, two adjacent parts have different positions of extinction. Tridymite may be cited as an example, because the 'arrow-head'-like crystals are twins, and the microsection in Fig. V.2c shows that when one half of the crystal is in the extinction position, the other half is illuminated.

(d) **When convergent light is used in conjunction with crossed nicols**, optical *interference figures* are often shown by mineral sections. These figures can be related to the difference in refractive index along the main crystallographic axes. Uniaxial crystals are those where the refractive index along only one axis is different; in biaxial crystals it is different along all three axes. The interference figures of these two groups are different, and they may be examined under high-power magnification either by inserting the Bertrand lens into the microscope or by removing the eyepiece. The ideal figures are shown in Fig. V.3. The uniaxial figure is composed of two isogyres, or black bands, intersecting centrally to form a cross, and radiating from the centre are a series of circles which are coloured unless monochromatic light is used. The biaxial figure again contains two isogyres, but these are now in the form of hyperbolæ situated in opposite quadrants of the figure. Once again circles are formed but now there are two sets, one at the centre point of each isogyre. Rings with large radii tend to fuse together to form lemniscates and finally ellipses. As the section is rotated on the stage, the biaxial interference figure changes and the isogyres form hyperbolæ of varying angles.

The interference figures of the uniaxial and biaxial crystals may be further differentiated into a negative and positive type, and they can be distinguished by observing the colour change produced in the interference figures when a mica or gypsum plate is inserted in the slot in the barrel of the microscope.

In biaxial crystals, the *axial angle* can be determined from the shape of the hyperbolæ made by the isogyres when they are at a maximum separation. When the isogyres remain almost completely together in the form of a cross during a rotation of the stage, the axial or $2V$ angle is near to 0° . With a little practice the axial angle can be estimated with a fair degree of accuracy.

The production of interference figures is not always easy, and satisfactory measurements can be made only when the mineral to be examined is present in large fragments which are not too thin. The ideal figures shown in Fig. V.3 are produced only when the crystal is inclined along a main crystallographic direction. If this is not the case, the figure may be difficult to identify, because the centre of the figure will be displaced away from the mid-point of the image. A microscope fitted with a universal stage is of great value, for by its use the crystal can be inclined until the figure is centralised.

Phase Contrast Microscopy is a recently developed technique which is proving of the greatest value in the examination of the thin sections of minerals. Briefly, a thin section of the sample is viewed under a single or crossed nicols, a specially designed plate of mica or similar material being inserted to alter the phase of the light. The internal features of some minerals are more clearly revealed and in many cases the crystal form of fragments is brought out. The value of the method in

FIG. V.2. PHOTOMICROGRAPHS OF THIN SECTIONS OF SOME CERAMIC MATERIALS
UNDER POLARISED LIGHT

- (a) a typical Welsh quartzite. ($\times 150$ magnifications)
- (b) a silica brick showing cristobalite. ($\times 800$ high contrast technique)
- (c) tridymite arrow-head twinned crystals in a silica brick. ($\times 800$)
- (d) a siliceous firebrick. ($\times 150$)
- (e) a high grade firebrick. ($\times 150$)
- (f) an aluminous firebrick. ($\times 150$)
- (g) a sillimanite refractory. ($\times 150$)
- (h) an alumina refractory. ($\times 150$)

FIG. V.3. IDEAL INTERFERENCE FIGURES OF MINERALS

- (a) Uniaxial and (b) Biaxial

FIG. V.4. PHOTOMICROGRAPHS OF SOME KAOLIN MINERALS

- (a) nacrite (b) dickite and (c) kaolinite. ($\times 500$)

FIG. V.5. ELECTRONMICROGRAPHS OF SOME KAOLIN MINERALS

- (i) kaolinite (ii) livesite and (iii) halloysite. ($\times 20,000$)
- (in every case *a* indicates normal, and *b* gold shadow treatment)

FIG. V.8. X-RAY POWDER PHOTOGRAPHS OF THE SILICA MINERALS

- (a) quartz (b) cristobalite and (c) tridymite

FIG. V.10. BACK REFLECTION X-RAY PHOTOGRAPHS OF COMPACTED ALUMINA
POWDERS

- (a) particles of 5 microns (b) particles of 0.5 microns

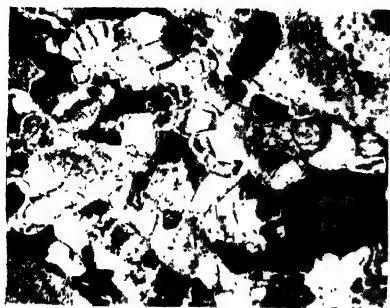


FIG. V.2. (a)

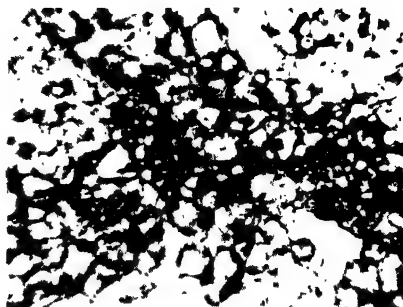


FIG. V.2. (b)



FIG. V.2. (c)

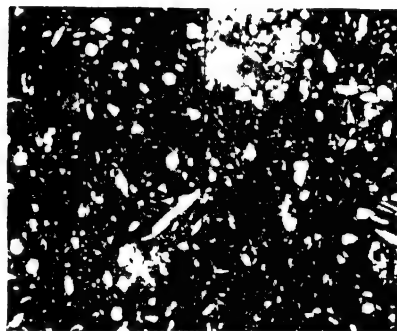


FIG. V.2. (d)



FIG. V.2. (e)

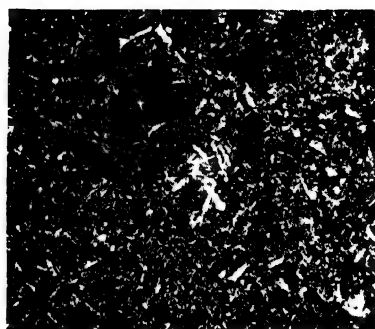


FIG. V.2. (f)

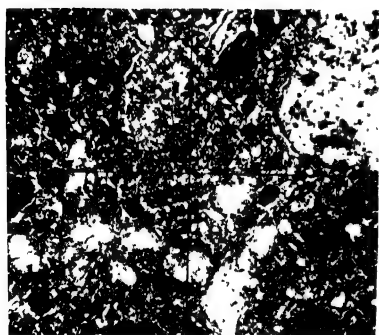


FIG. V.2. (g)



FIG. V.2. (h)

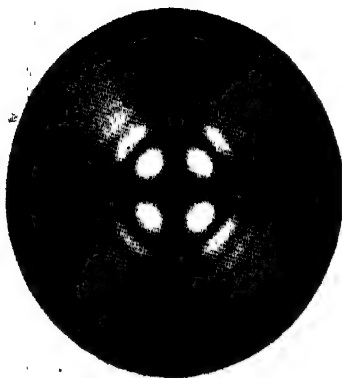


FIG. V.3. (a)



FIG. V.3. (b)

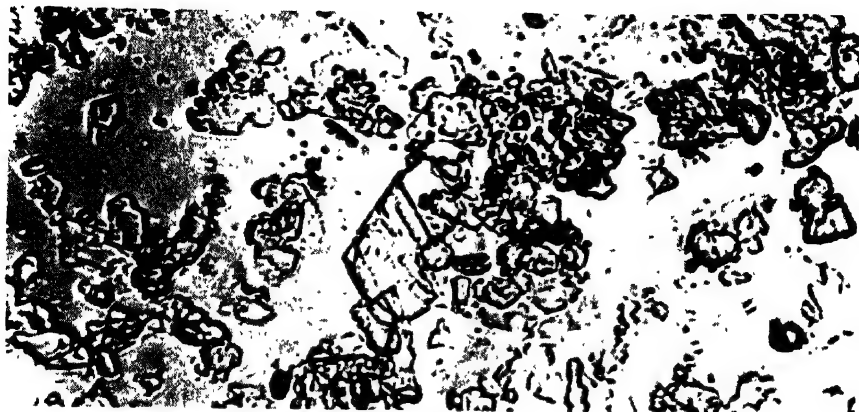


FIG. V.4. (a)

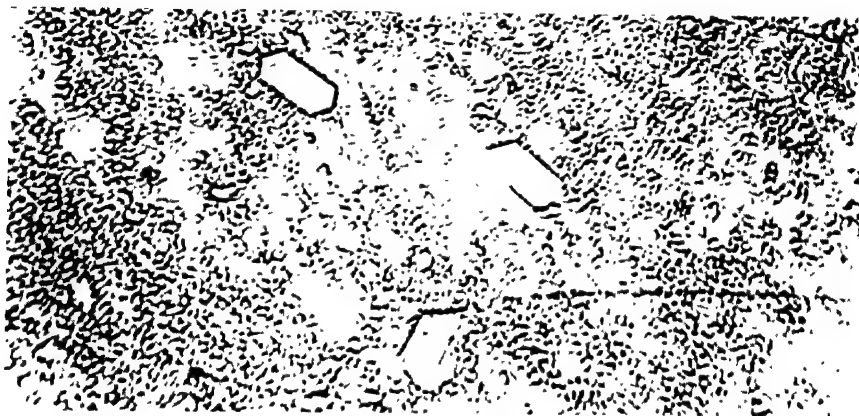


FIG. V.4. (b)

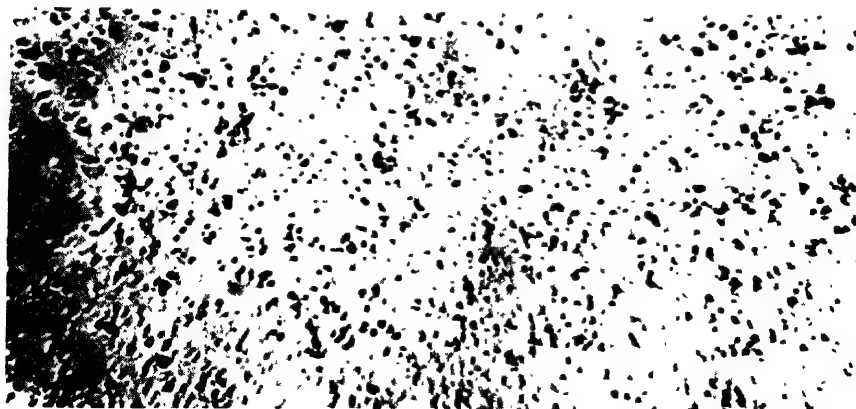


FIG. V.4. (c)



FIG. V.5. (a) (i)



FIG. V.5. (b) (i)

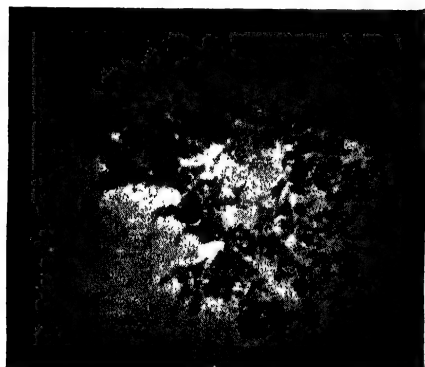


FIG. V.5. (a) (ii)

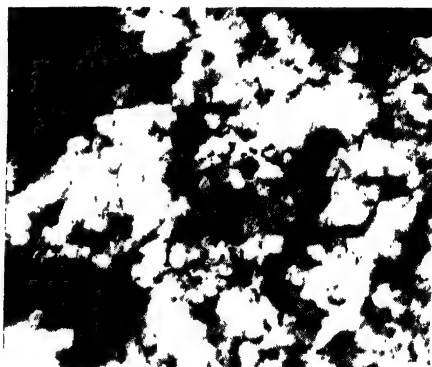


FIG. V.5. (b) (ii)

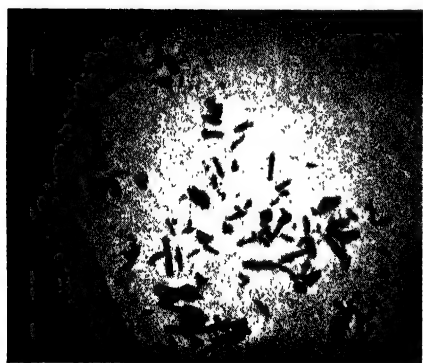


FIG. V.5. (a) (iii)



FIG. V.5. (b) (iii)



QUARTZ



CRISTOBALITE



TRIDYMIT

FIG. V.8.

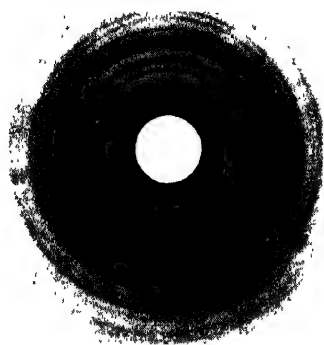


FIG. V.10. (a)



FIG. V.10. (b)

mineralogy has been demonstrated by Zernike¹ and Smithson² and undoubtedly the technique will have great application in the field of ceramic materials. Schoblik³ has applied phase contrast microscopy in studies of glaze discoloration.

A general review of new techniques in microscopy has been published by Vickers.⁴

EXAMINATION UNDER REFLECTED LIGHT

THE examination of opaque minerals is not possible by transmitted light, but the use of reflected light applied to the microscopic examination of materials has yielded information of very great value. The method is of particular importance in ceramic studies and has been the subject of a paper by C. Schouten.⁵

The section to be examined can be of any convenient thickness and only the top surface need be polished. Excellent results are sometimes obtained by cementing a thin sheet of clear glass to the section with Canada balsam so as to secure complete optical contact and a smoother surface than that produced by polishing, especially if the specimen is friable. Many modern microscopes are fitted with an attachment which projects a beam of light vertically downward on to the section; this light is then reflected upwards through the objective and measurements may be made in both ordinary and polarised light. The reflectivity of minerals is in direct proportion to their refractive index and this often provides a valuable means of identification. Reflected light examination offers additional advantages, but is complementary to, and not intended to replace the use of, transmitted light. More surface detail is revealed by its use, but the standard techniques of transmitted light microscopy are probably of more value in mineral identification.

In reflected light, some minerals in polished sections of ceramic materials can be readily recognised. Corundum (Al_2O_3), for example, always exhibits clear relief and the rounded grains of periclase (MgO) in basic materials are equally clearly shown. Spinel minerals, by contrast, show little relief and many silicates show none. Mullite crystals may often be recognised by their peculiar cross-sections. Defects in glazes and other ceramic bodies are often more conveniently studied in reflected light.

More detail may be revealed in a section to be examined in reflected light by etching the surface with a suitable chemical agent. Hydrofluoric acid, for example, attacks some silicates more rapidly than others and helps to differentiate various minerals.

The measurements of the optical properties of minerals, outlined in the previous pages, often enable those species to be identified. Tables have been compiled by various authors which contain the crystallographic data of all minerals so far identified. The appendix to this volume contains a list of the optical properties of some minerals occurring in ceramic bodies, which aid in their identification.

¹ Zernike, F., *Physica, Eindhoven*, 9, 686 and 974, 1942.

² Smithson, F., *Min. Mag.*, 28, 384, 1948.

³ Schoblik, A., *Speersaal*, 85, 95, 1952.

⁴ Vickers, A. E. J., *Research, Lond.*, 8, 17, 1955.

⁵ Schouten, C., *Trans. Brit. Ceram. Soc.*, 50, 185, 1951.

THE ESTIMATION OF MINERALS UNDER THE MICROSCOPE

IN the examination of ceramic materials by means of a microscope, a little of the powder or a thin section of the specimen is used; it normally consists of fragments of several minerals. The area of the thin section which is occupied by the particles of a particular mineral is in direct relation to the volume of that mineral in the original substance. Hence, the estimation of minerals under the microscope depends on the accurate measurement of the relative area of the fragments of the mineral. A rough estimation can be secured by using a squared micrometer plate in the eyepiece. The area occupied by the fragments of the mineral to be estimated can then be measured relative to the area of the total field under the microscope.

More accurate measurements are possible with the use of an integrating stage. The thin section is held in a carrier fitted with screws capable of moving the section in two directions at right angles. The screws are geared to a vernier graduated scale, so that the distance travelled by the stage can be accurately recorded. One edge of the section is set up along one of the cross-wires of the microscope, and the section is moved across the field of view by operating one of the screws. Most integrating scales are designed so that the graduated scale may easily be slipped in or out of gear. Consequently, when the edge of a fragment of the mineral which is being estimated coincides with the junction of the cross-wires, the scale can be geared to the screw thread. The scale records the distance traversed until such time as the mineral passes beyond the junction of the cross-wires, when it may be degeared. The same process is repeated when all other fragments are encountered whilst the section is passed across the field of view. The fraction of the total traverse which is occupied by the mineral gives the amount of that mineral by volume in the section across the field. A series of determinations at several positions along the length and breadth of the section must be made, and the mean result will be an accurate measure of the volume content of the mineral in the sample. Where the material being examined is of irregular composition throughout, several sections which are representative of the whole must be examined.

The estimation of minerals by microscopic means can be carried out with accuracy, provided that the grain size is large enough to be capable of reliable measurement and that the grain boundaries are clearly distinguishable. Needle-shaped minerals, such as mullite, are difficult to estimate, particularly if the particle size is small. In some cases, crystals are oriented along one particular direction in a sample, e.g. mica in slates and in some clays; reliable microscopic estimations can then only be made by taking samples along three directions in the material at right angles to each other and making determinations on thin-sections of these.

The identification and estimation of minerals by microscopic means depends largely on the size of the ultimate particles. The degree of magnification in an optical system is limited by the resolution of the lenses, and in practice, amplification factors of over 1,500 times are not easily attainable without resolution being lost. Consequently the optical microscope is not capable of identifying, let alone estimating, many of the minerals in clays, when particle sizes of less than 10μ are numerous.

Examination of Clays. When clay minerals can be obtained in a sufficiently pure state, some of their optical properties can be determined by preparing an oriented

specimen. The individual crystallites of clay and allied minerals are platy, consequently if they are allowed to fall freely in water, they tend to fall parallel to their largest face. If a microscope slide is inserted into a suspension of clay, the particles settle on to it with the basal sections of all fragments along the plane of the slide. Hence, a section of appreciable thickness and size can be built up, which behaves as though it were a single crystal. The mineral can be examined in ordinary and polarised light, and birefringence effects produced in the usual way. The results obtained are not so accurate as those using true single crystals, for the section is composed of a mosaic agglomeration rather than a continuous medium.

The optical properties of the kaolin minerals determined on oriented aggregates are given in Table V.II.

TABLE V—II. SOME OPTICAL PROPERTIES OF KAOLIN MINERALS

<i>Mineral</i>	<i>Optical Character</i>	<i>Mean Refractive Index</i>	<i>Birefringence</i>
Allophane	Isotropic	1.494	—
Halloysite	Biaxial negative	1.522	Small
Kaolinite	Biaxial negative	1.558	Small
Livesite	Biaxial negative	1.540	Greater than kaolinite
Nacrite	Possibly biaxial negative	1.560	Very small
Dickite	Possibly biaxial negative	1.562	Very small

The last two minerals, nacrite and dickite, form crystals which are large enough to be identified by high-power magnification. Microphotographs of these two are shown in Fig. V.4 along with kaolinite for comparison under the same conditions, facing p. 224.

Staining. Another useful technique for identifying small-sized particles of clay under the microscope involves the use of dyes or staining fluids.

Certain silicate minerals become *pleochroic* (see p. 222) when treated with dyestuffs. The adsorptive properties of clay minerals are well known, and a special method has been evolved for differentiating between the main types.¹

The dyestuffs (of which crystal violet, methylene blue, malachite green, safranin 'O' are the most useful) are dissolved in nitrobenzene and added to the powdered clay. Pre-treatment of the clay is essential to remove carbonates and iron oxides which might influence the results; a satisfactory method is to add two or three drops of dilute hydrochloric acid to a few milligrams of the sample on a microscope slide and, after a short interval, the liquid may be evaporated by gentle heat. When cool the dye solution may be added and a cover glass applied. Kaolin-type minerals adsorb all the dyes very readily and the pleochroic effect produced may be observed under high-power magnification.

Montmorillonite-type minerals not only adsorb the dyestuffs, but in certain cases change the colour of the dye. Malachite green, for example, is similar to litmus, and under acidic conditions undergoes a colour change to yellow. It must be emphasised that natural montmorillonites do not always exhibit this colour change, and it is important to treat the sample first with acid as described previously. If standard conditions are observed, it is easy to distinguish between kaolinite and

¹ Faust, G. T., *Report Invest. U.S. Bur. Mines.*, RX, 3522, 1940.

montmorillonite clays by stain tests. The method is also claimed to be of value in differentiating between some other clay minerals.¹

Although the optical microscope can be used with advantage in clay minerals studies, the extremely small particle sizes introduce severe difficulties. To observe some of the smallest of these particles a degree of magnification is required which is unattainable with optical systems.

ELECTRON MICROSCOPY

The Electron Microscope provides a means of high magnification without using an optical lens system. Furthermore, the source of radiation is not light but an electron beam of short wavelength; much better definition is obtained.

In this form of microscope a beam of electrons, emitted by a heated filament, is accelerated by an electric field and impinges upon a specimen. If the specimen consists of a composite powder or small particles of minerals which vary in thickness, the electron beam is attenuated differently over the whole field. Where there are no crystals, the beam is transmitted unaltered, but on passing through mineral fragments, the electrons will be adsorbed in varying degrees, and carry an image of the specimen which can be greatly magnified by passing the beam through a magnetic or electrical field, in which magnetic poles or electrically-charged plates replace the glass lenses in the optical microscope. The degree of magnification can be varied by increasing the charge on the plates, and magnifications of up to 60,000 times are possible.

The magnified image may be viewed directly by projecting the electron beam on to a fluorescent screen. Alternatively, a permanent record can be produced on a photographic plate or film.

The specimen has to be inserted in the barrel of the instrument, and is therefore at reduced pressure throughout; furthermore, the electron beam is intense, especially when high magnifications are being used, so great care must be taken to avoid disrupting or melting the specimen.

An electron microscope cannot be used to examine all the minerals in a raw clay, for these include particles of a wide grain-size range. The larger particles have to be removed by elutriation, and only those of less than 2μ examined. Clay mineral sections are normally prepared by dispersing a little powder in water, allowing the large grains to settle and applying a drop of the suspension to a collodion sheet. The water may then be evaporated and the sample is ready for analysis.

The electron microscope has revealed the fine structure of the smallest-particled clay minerals and is an excellent method for the identification of the principal types.

Clay minerals exist as plate-like or fibrous crystals and the method of specimen preparation automatically orients the particles along their basal section, so the thickness cannot be judged until they have been shadowed with a film of fine gold particles 'spluttered' from a filament under the influence of a strong electrical field. The particles moving at high velocities are allowed to impinge on to the surface of the section at a very small angle, so that a layer is built up against the side of the crystal,

¹ Mielenz, R. C., King, M. E. and Schieltz, M. C., Report No. 7, Amer. Petrol. Inst. Project 49 (Columbia Univ., N.Y., 1950).

directly in the path of the beam, thus forming a kind of shadow. If the angular projection of the particles is known, the thickness of the crystal can be calculated from the magnification factor of the microscope and the extent of the gold shadow. This 'gold-shadow' technique represents an important step forward in electron microscopy, as it enables sections to be examined with almost three-dimensional clarity (Fig. V.5*b* facing p. 224).

Photographs of kaolinite, halloysite and livesite are shown in Fig. V.5; those on the right were the result of the shadow technique, whilst those on the left were taken without any such treatment of the specimen.

Kaolinite is typified by hexagonal plates with a thickness to size ratio of about 1:12; halloysite is apparently lath-like in character; livesite is in the form of small plate-like particles with no well-defined crystal habit, and montmorillonite has a characteristic fibrous habit.

Recent investigations¹ into the crystal habit of halloysite have revealed that the lath-like crystals shown in Fig. V.5*b* (iii) are in reality rolled-up plates. Electron micrographs have been taken in the end-on position, and the hollow cylinder nature of the crystal established. Other samples show the tubular form of the plates along only a part of their lengths.

Montmorillonites exist as particles which are virtually single-layer; as more magnification power becomes available, the details of these individual units will be established, and, perhaps, the perplexing problem of the structure of these minerals may be finally solved.

X-RAY ANALYSIS

THE development and use of X-ray analysis has brought order into all branches of structural chemistry. Few have gained so much as the field of silicate minerals, which, prior to 1930, was a difficult and complex branch of science.

X-rays consist of electromagnetic waves, similar to light, but of much *shorter* wavelength (visible rays have a wavelength of $4\text{--}7 \times 10^{-6}$ cm. from violet to red, X-rays are between 10^{-7} and 10^{-9} cm. long). They are produced when a fast-moving stream of electrons impinges on a metal surface or target—termed an anticathode. They result from the energy liberated when the electrons of the metal atoms are 'excited' out of their normal orbits by the bombarding particles. The wavelength of the X-ray radiation so produced depends on the material of which the target is composed. Most metals emit a wide band of X-rays but with intense peaks at two characteristic wavelengths, termed K_{α} and K_{β} radiation, the value of which is related to the atomic number of the element (see p. 62).

Monochromatic X-rays can be produced if a material (termed a filter) is selected which transmits the K_{α} rays and absorbs the K_{β} . Copper K_{α} radiation, for example, can be produced by introducing a sheet of nickel foil into the beam, which effectively blocks the K_{β} rays. Table V—III indicates the filters which are used to give monochromatic radiation from other metal targets. When it is impracticable to use the filtering element in the form of foil, a sheet or film of a suitable salt is often satisfactory.

¹ Bates, T. F., Hildebrand, F. A. and Swineford, A., *Amer. Miner.*, **35**, 463, 1950.

TABLE V—III. CHARACTERISTIC WAVELENGTHS OF X-RAYS
EMITTED BY SOME METALS ($\times 10^{-11}$ cms.)

Metal	Aluminium	Chromium	Iron	Cobalt	Nickel	Copper	Molybdenum	Tungsten
K α	8320	2289	1936	1789	1658	1541	713	213
K β	7965	2081	1753	1617	1497	1389	631	184
Filter	—	Vanadium	Manganese	Iron	Cobalt	Nickel	—	—

When a parallel beam of either ordinary light or X-rays is passed through a very fine grating or a series of lines placed very close together, each line becomes the centre of an emerging spherical wavefront. As these cross similar wavefronts radiating from other lines, regions of darkness and brightness are produced depending on the phase relationships in the coinciding beams. This is known as a *diffraction pattern* and the spectral colours sometimes seen through a fine grating or a dusty window are given by white light with a wide range of wavelength radiation. When monochromatic radiation (i.e. of one wavelength) is used the colours are replaced by alternate regions of darkness and brightness. These patterns are produced only if the spacing of the grating is of a similar size to the wavelength of the radiation.

The atoms or ions in a crystal are arranged symmetrically (see Chapter II) and form planes or groups of planes within which there is a constant separation distance. These constitute a type of grating which will diffract radiation of a wavelength comparable to the distance between the planes. Most crystals have spacings between planes of their atoms corresponding to the wavelength of X-rays; consequently, characteristic patterns are produced and if these are suitably measured, the dimensions of the atomic planes and hence the structure of the crystal can be predicted.

In Fig. V.6 atoms, represented by dots, are arranged along planes p separated by a distance d . A monochromatic beam of X-rays, XY, impinges on these planes and makes an angle of θ with them.

The beam is made up of a series of waves which can be represented by X, X₁, X₂, X₃, . . ., etc. Each of these is reflected at different lattice points, and join together to move along YZ. The path lengths of each ray are different, and can be represented by XYZ, X₁Y₁Z, X₂Y₂Z, X₃Y₃Z, etc. If YN is drawn to cut X₁Y₁ perpendicularly at N, and X₁Y₁ is produced to O, where Y₁O is equal to Y₁Y, then OYN = θ .

The difference in path length between rays XYZ and X₁Y₁Z is clearly NO, because XY = X₁N and Y₁Y equals Y₁O.

$$\sin \angle OYN = \sin \theta = \frac{NO}{YO} = \frac{NO}{2d}$$

$$\text{therefore} \quad NO = 2d \sin \theta$$

By similar calculations, the path difference between X₂Y₂Z and X₁Y₁Z is also equal to $2d \sin \theta$ and so on.

If the distance NO is exactly equal to the wavelength (or to a whole number

multiple of the wavelength) of the incident radiation, all reflected waves along YZ will be of the same phase and the amplitude will be the sum of all the individual rays added together. Should λ not be exactly equal to the wavelength of the X-ray beam, each beam will be of different phase, and the net resultant amplitude from many reflections will be zero.

Only when θ has certain values will each ray be in phase and therefore, as the crystal is rotated, reflections will occur only when the relationship

$$n\lambda = 2d \sin \theta$$

is fulfilled, where $n = 1, 2, 3$, etc.

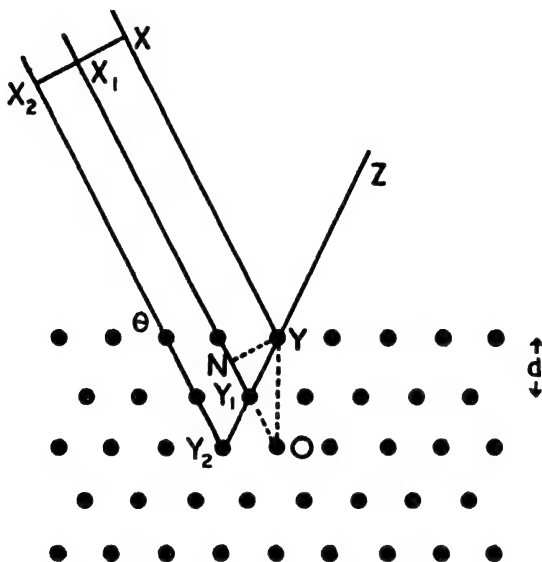


FIG. V.6. THE THEORY OF DIFFRACTION PATTERNS

This is known as the *Bragg relationship*, and it predicts that all planes in a crystal will reflect when inclined at certain angles to the incident beam, and that the angles (θ) depend on the wavelength of incident radiation (λ) and the distance between the planes (d). If the reflected rays are received on a photographic film or Geiger-Müller counter, a characteristic series of spots or lines, or electrostatic impulses is produced, the positions of which can be directly related to the positions of planes of atoms within the crystal lattice.

Each mineral can therefore be identified by its X-ray pattern which will be different from those of other minerals. In the Appendix to this volume, the principal lines of many of the minerals found in ceramic raw and fired materials are given. Clay minerals are generally characterised by patterns containing lines corresponding to large spacings. Kaolinites, for example, have strong reflections resulting from their basal spacing of about 7 Å; montmorillonites give lines related to their 14 Å spacing.

X-ray analyses can be carried out in a variety of ways depending on the type of specimen, the nature of X-ray radiation used and the camera employed.¹

The use of X-rays in ceramic studies² makes it practical to:

- (i) Ascertain whether a ceramic material is mainly crystalline or largely amorphous, even when it is composed of particles too small to be seen clearly under a microscope.
- (ii) Determine the structure of the lattice in any crystalline substance.
- (iii) Identify most crystalline minerals in a ceramic body.
- (iv) Estimate the proportions of one or more minerals in a substance under certain favourable conditions.
- (v) Measure (indirectly) the grain size of crystalline particles in a sample.

Preparation of the Specimen or Sample. When a sample to be analysed is in the form of a single crystal uncontaminated by impurities, much more information about the nature of its atomic configuration and the composition of the mineral can be deduced. The crystal may be aligned in the X-ray beam in such a way that reflections parallel to certain crystallographic axes can be recorded. The number of lines is then reduced, for only a limited group of planes within the crystal is able to satisfy the Bragg relationship. For example, a flake of mica oriented along its basal section will give only those reflections which correspond to the distance between the mineral sheets. The number of reflections may be increased by oscillating the crystal through a small angle. Eventually, the complete atomic configuration can be deduced by calculation from the planes of atoms which reflect at different incident angles of the X-ray beam.

The positions of lines or spots which appear in an X-ray pattern are determined by the arrangement of planes of atoms in the lattice, but the intensities of the reflections are dependent largely on the scattering power of the atoms which make up these planes. Therefore, the location of different atoms in the lattice can be established with great precision.

In most ceramic materials, the individual crystals are not large enough for single-crystal examination. This is particularly so with clay minerals, and most fired ceramic materials, because single crystals which can be isolated for analysis are not common. As in microscopy, oriented specimens can be prepared which may be analysed as a single crystal, but this method is restricted to clay minerals which are in a pure state.

The most common method of specimen preparation when the particle size is small, is to compact or mould the powdered material into a long fibre or rod. Satisfactory results are obtained only when the specimen is less than 0.5 mm. in diameter.

The powder may be packed into a thin-walled capillary tube of glass, but care has to be taken that the X-ray beam is not absorbed or scattered by the container. Silica glass tubes are the most satisfactory, but even this material is not entirely

¹ Klug, H. P. and Alexander, L. E., *X-ray Diffraction Procedures* (Hilger & Watts Ltd., London, 1954).

² Peiser, H. S., Rooksby, H. P. and Wilson, A. J. C., *X-ray Diffraction by Polycrystalline Materials* (Blackwell Ltd., Oxford, 1954).

suitable when low-angle lines are to be measured. One advantage of using capillary tubing is that the sample can be kept perfectly dry throughout; the tube may be sealed after filling, and the specimen thereby kept free from rehydration. This is of value when studying the decomposition products of certain minerals which lose water or carbon dioxide on heating, and readily reabsorb it on exposure to the atmosphere.

When such precautions are unnecessary, the specimen may be prepared by adding a little gum tragacanth to the powder, slightly wetting with water and then rolling it into a cylindrical shape between two glass plates. An alternative method is to attach the powder to a fine hair or fibre with a suitable adhesive. Successful specimens can often be made by extruding the material mixed with gum from a hypodermic syringe fitted with a needle of large bore.

A powder specimen is an aggregation of fine crystallites, usually with random orientation. An X-ray beam striking such a specimen will be reflected by all planes of atoms which are present in the minerals in the powder. To ensure this, the specimen should be rotated throughout the exposure, especially if the individual particles are relatively of large size. Except where only simple crystals are present, powder analysis photographs are difficult to interpret. It is impossible to restrict reflections to a small group of planes inclined at a certain angle to the beam. The lines which are produced by a mineral are, however, characteristic, and an X-ray photograph of a powder can establish the nature of the minerals present.

The X-ray pattern of a powder consists of rings and not spots, as is that produced by a single crystal. The reason is that whereas a certain set of planes in one crystal is at the same orientation to the incident beam throughout, the identical planes in crystals in the powder are inclined at many angles to the beam. Thus, for a given wavelength of radiation, a set of planes in a single crystal will produce one spot on a photographic plate (or set of spots corresponding to different angles of reflection for various orders), whilst those in a powder produce a ring formed from a merging series of spots, each with the same inclination to the direct beam, but radiating in the form of a cone from the specimen. The various orders of reflection give rise to other rings with different inclinations to the direct beam.

The X-ray Radiation. The wavelength of the radiation emitted from a target is determined by the nature of that target and the electrical potential applied between the filament and target. If that potential is low, only X-rays of a continuous range of wavelength are emitted. At a high potential, the electron orbits of the atoms of the target are disturbed and superposed on the continuous spectrum are peaks of high intensity at characteristic wavelengths.

The continuous wavelength form of X-rays is known as *white radiation*, and was used by the earlier workers in the field of X-ray crystallography. The peaks of maximum intensity are termed the *characteristic wavelength* of the target, and a list of the principal values has been given in Table V.III (p. 230). The use of suitable filters or a monochromator reduces or eliminates the background or continuous spectrum and all but one characteristic wavelength, thereby giving *monochromatic radiation*.

The analysis of single crystals using 'white radiation' is useful, for if measurements are made along one crystallographic axis, reflections will occur whenever $n\lambda = 2d \sin \theta$ (p. 231). A family of spots or lines will therefore result at characteristic

positions on a film placed behind the specimen; the resulting pattern is called a *Laue photograph*.

It is more usual, however, to use monochromatic radiation of a fixed wavelength. Copper K_{α} ($\lambda = 1541 \times 10^{-11}$ cm.) is commonly used, because a high intensity beam can then be used without serious deterioration of the target. If the specimen is rich in iron, considerable scattering takes place, and it is better to use a cobalt target in such cases. Molybdenum, iron and other targets are used according to the wavelength which is most suitable for the type of specimen being examined.

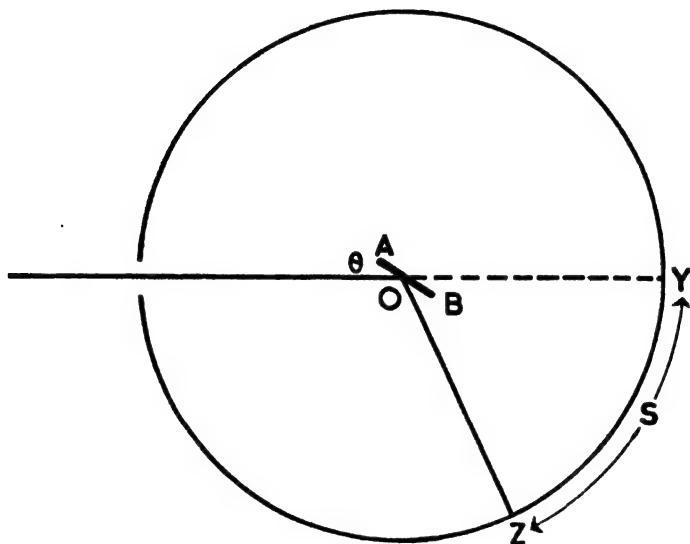


FIG. V.7. METHOD OF CALCULATING THE SPACING OF AN X-RAY LINE

X-ray Cameras, Structure Determination and the Detection of Minerals.

Many kinds of camera are designed specifically for structure analysis. Large crystals may be examined by means of a single crystal or Weissenberg goniometer. Attachments to these instruments enable a mineral to be set up along any crystallographic axis and the X-ray reflections are received on a photographic plate which is usually bent to form an arc of a circle with the specimen at the centre. Many modern cameras can be fitted with a Geiger-Müller counter which replaces the photographic plate. The accurate positions of spots can thus be located and the relative intensities determined directly.

The type of photograph obtained with a single crystal contains many spots and sometimes rings. It often shows a symmetrical pattern which is characteristic of the crystal form of the mineral. Powder samples may also be used in cameras of this type; the resulting photograph is a series of rings or ellipses radiating from the centre of the film.

There are special types of cameras designed specifically for powder specimens,

which are also satisfactory for mineral identification purposes. Such cameras are circular in shape, the specimen being located at the centre and rotated by a small electric motor built into the instrument. The X-ray beam passes through a collimator, impinges on the specimen, and the resulting reflections are recorded on a strip of film inserted round the perimeter of the camera. The diameter of the cameras may be of any size, although the two most generally used are 9 cm. and 19 cm. The smaller the camera the less will be the exposure time required, but the separation of lines along the length of the film will not be as great as with those of larger diameter. The film is in the form of strips, thereby saving photographic paper and enabling the camera to be reduced considerably in bulk. The photographic pattern produced is a series of lines which are, in reality, segments of rings. This line pattern is related directly to the spacings between the planes and the d value of a particular line can be calculated quite simply.

In Fig. V.7, AB represents the inclination of a set of planes in a crystal to the incident beam of X-rays. If the angle of incidence is θ and the reflected ray is along OZ, the angle ZOB must equal θ because the angle of reflection must equal the angle of incidence. Furthermore, the reflected ray OZ must satisfy the Bragg relationship $n\lambda = 2d \sin \theta$ where λ is the wavelength of the incident X-ray beam, and d is the spacing between planes parallel to AB.

By geometry the angle YOZ must also equal θ , therefore the angle YOZ equals 2θ .

The distance YZ is S or the separation of the line at Z from the direct beam, and OY is the radius of the camera.

$$\text{So} \quad \frac{YZ}{OY} = \frac{S}{r} = 2\theta \text{ (in radians)}$$

$$\therefore \theta = \frac{S}{2r} \text{ or } \frac{S}{D} \text{ where } D \text{ is the diameter of the camera.}$$

$$\text{Now} \quad n\lambda = 2d \sin \theta$$

$$\therefore d = \frac{n\lambda}{2 \sin \theta} = \frac{n\lambda}{2 \sin \frac{S}{D}}$$

All values on the right-hand side of the equation are known, or can be measured, therefore d (the spacing of the planes giving rise to the line at Z) can be calculated. The only difficulty lies in the accurate measurement of S , for the position of Y is uncertain. (Y is the centre-point of the unreflected beam which emerges from the camera.) If a small-diameter camera is used in which film completely encircles the camera (except for a small hole cut in the film to prevent fogging by the emergent beam), identical patterns are produced on each side of the direct beam; so, by measuring the separation between the same line on each side of the central point, the value of $2S$ is found.

In larger cameras, the normal practice is to use two strips of film. The emergent beam passes through a collimator, which prevents scattering. 'Stops' in the

ends of the collimator protect the films from the fogging effect of the unreflected beam. Consequently, there is a section of the perimeter of the camera, close to the direct beam, which is not covered by film. This distance can be measured and hence positions of lines on the photographic film calculated as before.

For accurate analyses, the positions of lines on the film should be measured by a vernier microscope and then converted to d -values. When many determinations have to be made, and only details of the minerals present in a sample are required, a very useful labour-saving calibration chart can be made from a strip of celluloid or perspex, of similar size to the film-strip, marked off in d -spacings which have been calculated from the dimensions of the camera and the wavelength of the incident radiation. The lines on a photograph of an unknown mineral may then be estimated directly in d -values by comparison with the calibrated strip.

The identification of minerals by X-ray analysis is comparatively easy and rapid, and the method is of value in many ceramic investigations. Fig. V.8 shows the characteristic X-ray patterns of the three silica minerals, quartz, cristobalite and tridymite. Although some lines are common to all, certain reflections are unique to each of the crystallographic types (see facing page 224).

One feature of most X-ray powder cameras is that the collimator at the emergence side is so designed that lines corresponding to a d -spacing of greater than 7 Å cannot be recorded. X-rays are scattered to some extent by air particles, therefore the unreflected rays may be deflected slightly from their normal parallel path; the emergent beam would be spread over a comparatively large area, and reflections at low angles would be masked or obliterated by fogging if a collimator were not used. This is usually of little consequence as most minerals do not have spacings greater than 7 Å, but it is a serious drawback in clay mineral analysis where planes with separations up to 25 Å may be present.

Cameras for studying the X-ray patterns of clay minerals must be capable of revealing reflections which are at small angles to the direct beam. The removal of the exit collimator, or the design of a camera without one, is a simple matter, but the problem of eliminating low angle scattering still remains. A commercial 19 cm. camera from which the exit collimator has been removed is suitable if the scattering caused by air molecules is reduced by completely evacuating the camera. Spacings of 35 Å can be detected without any noticeable contamination by random radiation, provided that the pressure in the camera is lower than 1 mm. Cameras of 9 cm. and 19 cm. diameter have been modified in this way, but the larger size is preferred because this gives a greater separation of lines.

Low angle scattering may also be reduced by replacing the air in the camera with hydrogen.

Because the arrangement of the atoms in all layer lattice silicates is similar, most of the lines in the patterns of these minerals are common to all. Ionic replacements may cause a slight shift in the line from a particular d -spacing, but the same characteristics can usually be observed in all minerals. The basal spacings of layer lattice minerals, i.e. the distance between identical planes of atoms in two successive layers, are different, and reflections from such planes are characteristic of the mineral type. The principal line corresponding to the d -spacing of the basal section for the layer lattice minerals is as follows:

7 Å (invariant)	Minerals of the kaolin group
10 Å (invariant)	Micas and hydrous micas
14 Å (invariant)	Chlorites
14 Å (reduced to 11.8 Å by heat treatment at 110° C.)	Vermiculites
14 Å (increased to 17 Å or above by treatment with glycerol)	Montmorillonites

The values given are only approximate and differ slightly for particular minerals in any one group.

The best means of studying minerals with these long spacings is with a camera of the Brindley focusing or semi-focusing type. Details of the technique are given in *X-ray Diffraction by Polycrystalline Materials* by Peiser *et al.* (see p. 232).

From the examples shown, it is obvious that a complex line pattern is produced by any one mineral. Each line is characteristic of a set of planes in the crystal, and there may be as many as fifty of these recorded on one photograph. The identification of any mineral does not present much difficulty, provided that it is in a fairly pure state. Ceramic materials, however, may contain many minerals, each of which has its own characteristic line pattern. The X-ray pattern of a composite mixture of minerals may therefore be highly complex and difficult to interpret. Some minerals are of variable composition, and isomorphous substitution and solid solution are common phenomena in minerals associated with ceramic mixtures. The X-ray pattern of such minerals may vary considerably between different samples, and although such variation may be indicative of the degree of substitution when the pure mineral is examined, in a composite mixture the change in pattern may be confusing.

Despite these difficulties, X-ray analysis is the quickest and most positive method available for the detection of many minerals. A complex ceramic material would usually be analysed using the powder technique described in the preceding pages, so that a line pattern is obtained containing the characteristic reflections from each mineral present. A comprehensive index of the *d*-spacing for all known minerals has been drawn up by the American Society for Testing Materials, Philadelphia, U.S.A., and it is by reference to this, or to a similar Table, that the minerals present in an unknown material may be identified. The *d*-spacings corresponding to the three strongest lines of many minerals in ceramic bodies are given in the Appendix.

If one mineral predominates in the sample, the strongest lines in the pattern will probably be characteristic of this mineral, hence its identification is a comparatively easy matter. The remaining lines can then be catalogued and other minerals established by referring to the Index.

When no one mineral predominates, the indexing of the lines in a pattern is complicated and is largely a matter of trial and error. The task can often be simplified if the approximate composition or the previous history of the sample is known. The characteristic line patterns of only those minerals which can be present, need be examined and compared with the lines from the unknown sample.

If many mineral analyses by X-ray methods are contemplated, it is advisable at

the outset to prepare a set of line patterns of the important minerals occurring in ceramic bodies and comparing these, in turn, with the pattern of the substance being examined. Much tedious measurement can be avoided by this procedure.

An important development in the use of X-rays in ceramic studies has been the introduction of *high temperature techniques*. The progress of reactions as they take place can be observed and the phases present in a fired mixture can be identified without prior cooling and the consequent chance of further reaction.

High temperature cameras are usually of conventional type, designed to take powder specimens and fitted with a heating element. Johnson¹ has described a simple tantalum resistance heater capable of maintaining a specimen at 2200° C. A further modification is a detachable film holder which enables a series of photographs to be taken of a specimen whilst it is maintained at a high temperature.

Jay² was one of the early pioneers in the field of high temperature X-ray techniques applied to ceramic materials. He studied the changes in the lattice constants of quartz from room temperatures to above the inversion point. Johnson and Andrews,³ using the same method, have studied the inversion and thermal expansion of cristobalite.

High temperature X-ray techniques are not yet firmly established. Although several commercial cameras are capable of being operated at temperatures up to 1500° C., the interpretation of the results which they give is often not an easy matter. One great difficulty is the correct assessment of the temperature of the specimen being analysed and no entirely satisfactory method, of general application, has yet been found. A critical survey of high temperature X-ray methods has been published by Brand and Goldschmidt.⁴

THE ESTIMATION OF MINERALS BY X-RAY METHODS

THE identification of minerals by X-ray analysis is based upon the spacings of the characteristic line pattern. The intensity of the reflections depends upon the arrangement of atoms in the crystal, the number of reflecting planes and the intensity of the X-ray beam. If the radiation can be controlled, the intensity of lines, for a certain crystal, will be in proportion to the number of reflecting planes, or, in other words, to the amount of that mineral present in the sample.

The intensity of radiation is difficult to regulate, for although it is largely dependent on the electron stream impinging on the target and the potential across the X-ray tube, other factors (such as the condition of the surface of the target) have an influencing effect. Furthermore, minerals vary considerably in their relative scattering or absorptive power to X-rays, so the nature of the contaminant may alter the intensity of the line-pattern of a particular mineral.

The *estimation* of minerals is not possible, therefore, by comparing intensities produced under normal exposure conditions.

There are two methods, however, each widely used, which permit the quantitative analysis of certain minerals by X-ray means. If quantitative methods of X-ray

¹ Johnson, J. R., *J. Amer. Ceram. Soc.*, 37, 360, 1954.

² Jay, A. H., *Proc. Roy. Soc.*, A.142, 237, 1933.

³ Johnson, W. and Andrews, K. W., *Trans. Brit. Ceram. Soc.*, 55, 227, 1956.

⁴ Brand, J. A. and Goldschmidt, H. J., *J. Sci. Instrum.*, 33, 41, 1956.

analysis are to be successful and accurate, the first essential is to measure the total intensity during an exposure; this may be achieved either (a) directly, or (b) relatively, and both methods are used extensively.

(a) The Geiger-Müller counter is a type of electrostatic voltmeter, which can be used for measuring the intensity of X-ray radiations. Many cameras are designed so that the counter can be mounted on a moveable arm, and used in place of a photographic film. A motorised drive moves the counter through an arc of a circle centred on the specimen. As each reflected ray is encountered, the intensity of the beam is recorded directly on a microvoltmeter and the positions of the reflections and their absolute intensity are determined in one operation.

The intensity measured by the Geiger-Müller counter is, in the simplest terms, the X-ray flux falling on the instrument per unit time. A particular reflection which is characteristic of the mineral to be estimated, is allowed to fall on the counter, and the resulting deflection on the voltmeter is measured. The counter is then adjusted to measure the intensity of the direct beam, or a small fraction of it. Duplicate measurements may be carried out and the relative intensity of the reflection to that of the direct beam estimated.

If a series of standards is compiled containing different known percentages of minerals to be estimated, the amount of a particular mineral in an unknown sample can sometimes be determined.

(b) When a Geiger-Müller counter is not available, quantitative measurements can be made by measuring the intensity or density of the corresponding lines on a photographic film by means of a microphotometer, which is usually of the photoelectric cell type. A beam of light is projected through the line on the film and the density determined by measuring the microvoltage produced in a photocell. Unfortunately the density of a line on a photographic film, as measured by a microphotometer, is not directly related to the intensity of the reflected ray which produced it. This is due to a variety of reasons but it depends mainly on the nature of the film and the development conditions. The difficulties can be largely overcome by the use of a calibration strip which compares the intensity of radiation with the density of the film.¹ This strip is usually printed on the margin of each film exposed, so that any variations in the developing process may be automatically corrected. These standard exposure strips are produced by rotating a specially-designed sector wheel in the X-ray beam, and allowing the transmitted beam to fall only along the edge of the film.

Once the calibration strip has been made, the density of a line in the X-ray pattern can be related directly to the intensity of radiation which produced it.

Small variations of X-ray intensity cannot be avoided during long exposures because of fluctuations in operating conditions and irregularities in target emissions, so that it is not possible to compare the intensity of radiation of a characteristic line with a series of standards, and so deduce the amount of mineral present. This difficulty is not serious when a Geiger-Müller counter is employed, as the intensity of a reflected ray can be assessed in a few seconds and compared immediately with the direct beam, but with a photographic film, comparatively long exposures are required to produce a line pattern of sufficient intensity. For example, a crystalline

¹ Bunn, C. W., *Chemical Crystallography* (Oxford U.P., 1945).

material such as quartz, requires an exposure of about 45 minutes using a 9 cm. camera and copper K_{α} radiation at 50 kV and 20 milliamperes. Clay minerals require 4 hours in a 19 cm. camera under the same conditions to produce a suitable photograph.

A neat method of compensating for these variations is to use an *internal standard*. The sample of powder to be analysed is mixed with a prearranged amount of some known mineral. The resulting X-ray pattern will contain the reflections of the mineral superimposed on that of the sample. The relative intensities of characteristic lines in the mineral to be analysed may then be compared with the intensity of a line or lines in the added mineral. As an example, in the estimation of quartz using fluorspar as the internal standard described by H. M. Richardson,¹ standards are first prepared by mixing quartz with fluorspar in different proportions. Quartz has a strong characteristic X-ray reflection at 3.35 Å and fluorspar one at 3.15 Å. The relative densities of these two lines in a series of photographs of quartz-fluorspar mixtures of known proportions can be assessed and plotted graphically and a calibration graph prepared.

An unknown sample of quartz may be analysed by adding a known amount of fluorspar and comparing the relative densities of the characteristic lines. The amount of quartz can be estimated directly from the calibration graph.

There are several factors which may either reduce the accuracy or even prevent a quantitative determination being made:

(i) For instance, no other mineral must be present in the sample which gives a reflection near to the characteristic line of the mineral being estimated and that of the standard mineral. Mica, cristobalite and tridymite, when associated with quartz, restrict the use of this method when fluorspar is used as the internal standard.

(ii) Another source of error is that the line-pattern of a mineral is influenced by the size of the crystallites. As the particle size decreases, the X-ray reflections broaden and the photometer curve of a line-pattern altered in this way shows an increase in the base of the 'peak', and a reduction in magnitude. For this reason, it is better to measure the relative areas of the peaks in the intensity curve rather than the heights.

This method proved useful for estimating the mullite content of mixtures of amorphous silica and alumina fired to different temperatures. Quartz was used as the internal standard, and the 4.21 Å line of this mineral compared with the mullite line of 5.4 Å. Neither of the components of the mixtures was contaminated with quartz and no other minerals were produced which interfered with the lines to be measured.

Fig. V.9 shows the type of photometric curve produced by measurement of the X-ray pattern in the region of the two lines. Superimposed on the mullite line is the trace of a 'peak' which appeared after light firing when presumably the mullite was of small grain size. The broad base line and the shallowness may be compared with that of the full curve, which represents a more crystalline mullite.

The quantitative estimation of minerals by X-rays is accurate to about ± 5 per cent when the conditions of testing are ideal; i.e. when the mineral to be estimated

¹ Richardson, H. M. and Wild, F. G., *Trans. Brit. Ceram. Soc.*, 51, 398, 1952.

and the internal standard used have characteristic reflections far removed from those of contaminants.

A further requirement is that the mineral being estimated should be available in a pure state so that a calibration graph can be constructed. Only reflections with a strong intensity should be selected for quantitative measurement. Weak lines of a pure mineral will be fainter still when diluted with impurities, and are then of little value.

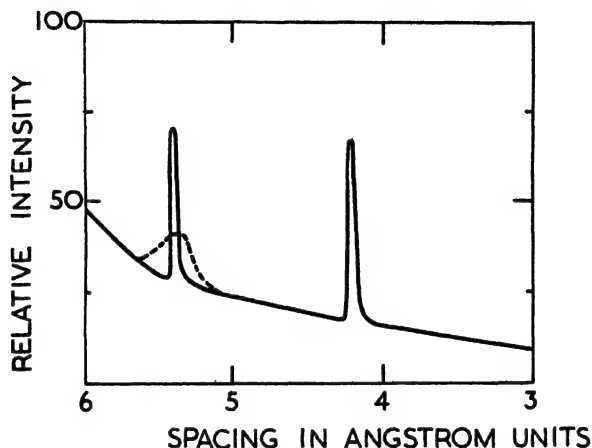


FIG. V.9. A PHOTOMETRIC CURVE OF THE LINE PATTERN OF A MIXTURE OF MULLITE AND QUARTZ

THE DETERMINATION OF CRYSTALLITE SIZE BY X-RAYS

If the X-ray powder photographs of crushed specimens of the same mineral but of different crystallite size are compared, a change is observed as the size decreases, from a set of spots, through lines, partially continuous and partially spotty, to complete lines of uniform intensity. The degree of 'spottiness' of the pattern is an index of the crystallite size and if uni-sized particles are present, a fair measure of their dimensions may be calculated. With small particles, the sharp rings characteristic of particular reflections of the mineral become banded or diffuse (see Fig. V.10) and the spread of the lines can also be related to the crystalline size. Exceptionally fine particles give rise to diffuse bands or haloes at low angle, which may be observed surrounding the direct beam and at a small separation from it.

The limits of crystallite size which produce spots, rings, diffuse bands and low-angle haloes, vary with the type of mineral and the degree of crystallinity. Wherever possible, standard photographs should be compiled from materials of known size.

Particle size determinations by X-ray methods are more conveniently made by using a *back-reflection technique*. The specimen to be tested can be in almost any form, but the best results are obtained on a large fragment or on a compressed powder with one face freed from irregularities. A narrow monochromatic beam of X-rays is projected on to this face, and is reflected *back* at characteristic angles on to a

photographic plate or film. By this means, a pattern is produced by reflections from the planes of atoms in the minerals of the specimen, and the d -spacings can be calculated. The film, which is set parallel to the reflecting face of the specimen, is usually flat and the incident X-rays pass through a small hole in it. The distance between the specimen and the film can be adjusted to give the most convenient separation of the lines.

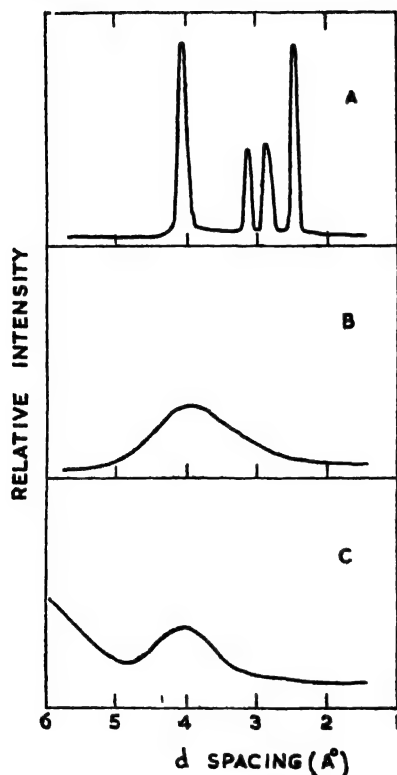


FIG. V.11. PHOTOMETRIC CURVES OF THE LINE PATTERNS OF (A) CRISTOBALITE; (B) FUSED SILICA; (C) SILICA GEL

(showing the line broadening and the development of low-angle haloes as the crystallite size decreases)

The particle size of the mineral being analysed is determined by examining a characteristic ring. The size of a spot in such a ring is related to the dimensions of the crystal which produced it; so that a size count of all spots in a particular ring can, by suitable calculation, or by comparison with standard samples, be converted into a particle size distribution.

Fig. V.10 *a* and *b*, shows the type of photograph obtained from samples of α -alumina (corundum). The difference between powders of different particle size is most marked (facing p. 224).

Back reflection photography may also be used for small particles because the line broadening is well-defined, as also is the low-angle scattering. This is illustrated by Fig. V.11 *A*, *B* and *C*, where samples of silica of different crystalline development are compared.

The calculation of the grain size of a powder from the line broadening and low-angle haloes is rather complicated, and the reader should refer to an article on the subject by K. L. Yudowitch.¹

ELECTRON DIFFRACTION

THE technique of electron diffraction is similar to that of X-ray diffraction, but a beam of electrons is substituted as a source of radiation. Most modern electron microscopes are readily adapted for this purpose.

The modern concept of the electron is expressed as a wave mechanical function. Instead of a rigid particle, a wave motion is postulated but the wavelength is very short. The atoms in a crystal diffract such radiation, and the Bragg relationship $n\lambda = 2d \sin \theta$ applies. As a consequence, a certain d -spacing will give rise to a reflected ray at a much smaller angle than when X-rays are used.

Electron diffraction is of great value in the structure analysis of complex crystals, because reflections corresponding to smaller planar spacings can be detected. More precise positioning of atoms in a complex lattice is therefore possible, although other technical factors have so far limited the application of electron diffraction.

INFRA-RED METHODS

INFRA-RED spectroscopy and spectrometry also involve the use of radiation, but of much *longer* wavelength than that of visible light. The wavelength range of the spectrum classified as infra-red, ranges from 0.75–300 microns (1 micron = 10^{-4} cm.), but the important region for studying minerals and crystals is the region 2.9–16.7 microns, or as it is more commonly expressed, in the frequency range of 3500–600 cm^{-1} .

Molecular groupings within a crystal often have characteristic vibrations which are accompanied by a change in dipole moment. For example, in a silica tetrahedron, where a silicon cation is at the centre of four oxygen anions, vibrations cause a shift of the positively-charged silicon, relative to the negatively-charged oxygens. When radiation of the same frequency as the vibration is passed through the crystal, the radiation is absorbed, so by subjecting a mineral to a range of monochromatic radiation frequencies, several absorption bands can be recorded. Molecular vibrations with frequencies corresponding to the infra-red radiation are common, and hence the absorption spectra in this region is indicative of atomic grouping within a crystal.

Certain groupings, which are common to many minerals, give characteristic absorption bands. For example, a hydroxyl group ($-\text{O}-\text{H}$), strongly absorbs radiation of frequency about $3500^{-1} \text{ cm}^{-1}$; the carbonate radicle has bands of absorption at frequencies of $1450^{-1} \text{ cm}^{-1}$, 880^{-1} cm^{-1} and 730^{-1} cm^{-1} . Similarly, an $\text{Al}-\text{O}$ and a $\text{Si}-\text{O}$ group will also absorb at specific radiations, hence the infra-red spectrum of a mineral is made up of a series of absorption bands of characteristic frequencies.

Quite often a mineral in a complex mixture can be identified by its infra-red

¹ Yudowitch, K. L., *J. Applied Physics*, 20, 174, 1949.

absorption and, in certain cases, the degree of absorption at a particular frequency may be indicative of the amount present.

The source of infra-red may be a glowing filament or a hot silicon carbide rod, both of which emit radiation over a wide range of frequency. The infra-red beam passes through a collimator to the specimen which should be in the form of a thin film. The transmitted rays then pass through a system of mirrors on to a rock salt prism which can be rotated, so as to vary the frequency of radiation received on the detector. The magnitude of the spectra over the wavelength range is measured on a thermopile or bolometer, and is recorded continuously on a potentiometer.

Most infra-red spectrometers work on the split-beam principle, for the intensity of incident radiation is apt to vary over the wavelength range. One half of the beam passes directly through the sample, whilst the remainder is transmitted directly on to the mirror system. The two beams are recorded simultaneously and the difference in intensity at any point represents absorption by the specimen.

Rock salt is commonly used for specimen mounts and the reflecting prisms because it is one of the few materials which do not absorb infra-red radiation over most of the wavelength band.

There are many references to the use of infra-red methods for the identification of minerals. In a recent publication of the American Petroleum Institute¹ a section is devoted to characteristic absorption spectra of minerals associated with ceramic raw materials.

Clays have proved most difficult materials from which to obtain satisfactory infra-red absorption pattern. Because the crystallite size of such materials is small, specimens for analysis have to be composed of agglomerates, with the result that considerable internal reflections occur and a consequent substantial reduction in the intensity of the transmitted beam. Auskern and Grimshaw in, as yet, unpublished work, have shown that satisfactory transmissions are possible if the clay samples are mounted in a cold-pressed potassium bromide pellet. The absorption region in the hydroxyl range, i.e. 2.7–3.2 microns is best studied by using either a lithium fluoride prism or a diffraction grating in place of a prism.

THERMAL ANALYSIS METHODS

THERMAL analysis methods are based on the observation or measurement of the heat changes which occur when a material undergoes physical or chemical changes on being heated or cooled. All reactions involve an energy change which is usually manifested as a thermal effect, and are termed *exothermic* when heat is evolved, and *endothermic* when heat is absorbed. This principle has been known for many years, and is a recognised means of studying the structural changes which take place in metal systems at different temperatures. Early workers in the field of thermal analysis closely copied metallurgical methods and observed the inflections in the temperature rise when a material was heated under uniform conditions.

The technique was first applied to clays in 1887, when H. Le Chatelier² studied

¹ *Infra-red Spectra of Reference Clay Minerals*, American Petroleum Institute, Research Project 49 (Columbia Univ., N.Y., 1951).

² Le Chatelier, H., *Bull. Soc. Min.*, 10, 204, 1887.

the thermal characteristics of aluminosilicates and attempted to classify them by this means. Similar work was carried out by H. Wallach¹ in 1913, who indicated how certain minerals could be identified by their thermal behaviour. S. Satoh² also used the method for investigating various kaolins; whilst in his comprehensive study of the reactions taking place when clays were heated, J. W. Mellor³ demonstrated the endothermic and exothermic effects characteristic of kaolinite and a wide range of other clay minerals.

J. W. Cobb and H. S. Houldsworth⁴ were amongst the first to apply the method of *differential* thermal analysis, in which the temperature of the test material is measured relative to that of an adjacent inert material, instead of to that of the furnace. A thermocouple embedded in the test-piece and another in the inert material are connected in opposition, so that any appreciable E.M.F. set up during the heating results from the evolution or absorption of heat in the test sample. This technique forms the basis of all modern methods of thermal analysis.

From about 1935 onwards, the method gained in favour and began to be increasingly applied in mineralogical studies of clays and related silicates; by J. Orcel and S. Caillère⁵ in their investigations on montmorillonite minerals; on clays, laterites and bauxites by J. Orcel;⁶ on kaolin minerals by H. Insley and R. H. Ewell;⁷ on talc by R. H. Ewell and co-workers;⁸ and on pyrophyllite by E. Thilo and H. Schunermann.⁹ F. H. Norton's work¹⁰ in 1939 showed the possibilities of an improved method for identifying and estimating clay minerals, after which it was extensively employed by American mineralogists¹¹ and soil chemists.

Grimshaw, Heaton and Roberts¹² studied a wide range of British clays and allied ceramic materials, and the technique is now standard practice in many laboratories and industrial concerns where routine control of raw material is essential.

With greater refinements in procedure and the standardisation of equipment, differential thermal analysis has become a valuable method, not only in the identification of minerals in complex mixtures, but also as a quantitative measure of mineral content in many cases.

Apparatus. In the apparatus developed by Grimshaw and Roberts, a fixed weight of the sample (about 0.8 gm.) is packed into one cubical compartment of a thin-walled refractory container (Fig. V.12), the other compartment being filled with an inert material which has no thermal reaction over the range of temperature of the test. This specimen holder, which is made of sintered alumina, fits into the lower half of a refractory block, the lid of which completes the cylindrical shape,

¹ Wallach, H., *Comptes Rendue*, 157, 48, 1913.

² Satoh, S., *J. Amer. Ceram. Soc.*, 4, 182, 1921.

³ Mellor, J. W. and Holdcroft, A. D., *Trans. Eng. Ceram. Soc.*, 10, 94, 1911.

⁴ Houldsworth, H. S. and Cobb, J. W., *Trans. Eng. Ceram. Soc.*, 22, 111, 1923.

⁵ Orcel, J. and Caillère, S., *Comptes Rendue*, 197, 774, 1933.

⁶ Orcel, J., *Comptes Rendue*, 183, 565, 1926.

⁷ Insley, H. and Ewell, R. H., *J. Res. Nat. Bur. Stand.*, 14, 615, 1935.

⁸ Ewell, R. H., Banting, E. N. and Geller, R. F., *J. Res. Nat. Bur. Stand.*, 15, 551, 1935.

⁹ Thilo, E. and Schunermann, H., *Z. anorg. Allgem. Chem.*, 230, 321, 1937.

¹⁰ Norton, F. H., *J. Amer. Ceram. Soc.*, 22, 54, 1939.

¹¹ Kauffman, A. J. and Dilling, E. D., *Econ. Geol.*, 45, 222, 1950.

¹² Grimshaw, R. W., Heaton, E. and Roberts, A. L., *Trans. Brit. Ceram. Soc.*, 44, 69, 1945.

thus enabling it to be used in a tubular wire-wound furnace. The square end-section facilitates the handling of the block and provides a means for its location in the furnace.

Thermocouples, which are usually of fine-gauge (28 s.w.g.) chromel-alumel wire,¹ are arranged in the specimen holder as shown in Fig. V.12. A chromel-to-alumel junction is located in the centre of both the test and the inert sample compartments. If these are regarded as separate thermocouples, the principle of differential thermal analysis can be clearly appreciated. The junctions in the two

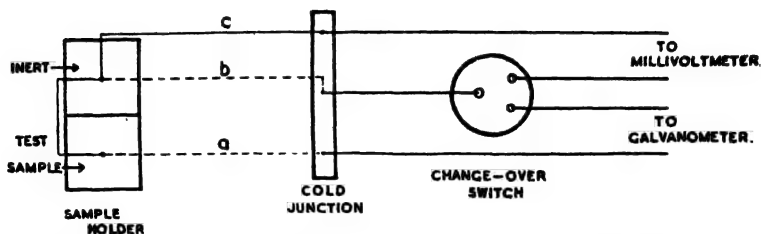


FIG. V.12. DIFFERENTIAL THERMAL ANALYSIS APPARATUS. THE SPECIMEN HOLDER AND THERMOCOUPLE ARRANGEMENT

compartments are identical in all respects, therefore if they are both at the same temperature an E.M.F. will be generated in both circuits, the voltages of which will be exactly the same and current will flow in the same direction, i.e. chromel to alumel, in each. These conditions apply independently of the actual temperature of the junctions. When the junctions are connected as shown in the diagram with the alumel wire common to both, the potential difference generated at one junction will be equal to but in opposition to that at the other and the net reading on a galvanometer connected across the circuit-leads *a* and *b* will be zero at all temperatures of the specimen holder. If, however, there is a difference in temperature between the sample compartment and that of the inert, the E.M.F. in the two thermocouples will differ and a net potential across the leads *a* and *b* will result, which will be a measure of the *difference in temperature* between the two junctions. The actual temperature at any time is given by connecting the leads *b* and *c*, which are respectively chromel and alumel, to a millivoltmeter through a change-over switch.

The refractory block is of alumina or mullite fired to a high temperature to give strength to the moulded shape. The specimen holder rests in a depression cut near the end of the lower half, and three holes are drilled in the body of the block through which pass the thermocouple leads. The edges of the lower half are raised slightly and a complementary taper is removed from the lid in order to give a better fit and to ensure that the specimen holder is totally enclosed (see Fig. V.13).

Both the block and specimen holder are now made commercially, and consequently identical sets can be used by different laboratories and results may be directly compared.

¹ Chromel-alumel thermocouples are preferred because of the large thermo-E.M.F. of this metal combination. Platinum-platinum/rhodium couples are sometimes employed because they can be used to higher temperatures (1250-1300° C.) with greater stability although their sensitivity is five or six times less.

The use of blocks and specimen holders made of refractory material confers many advantages over the metal type used by some workers. The temperature differences when exo- or endo-thermic changes take place in the test sample are greater and are defined more sharply, because the heat transfer between the test sample and the surrounding material is slower as a result of the lower thermal conductivity of the refractory block. Furthermore, a block and specimen holder made from alumina or mullite is free from corrosion or oxidation and permits tests to be carried out at temperatures well above 1000°C. , which is difficult or impossible

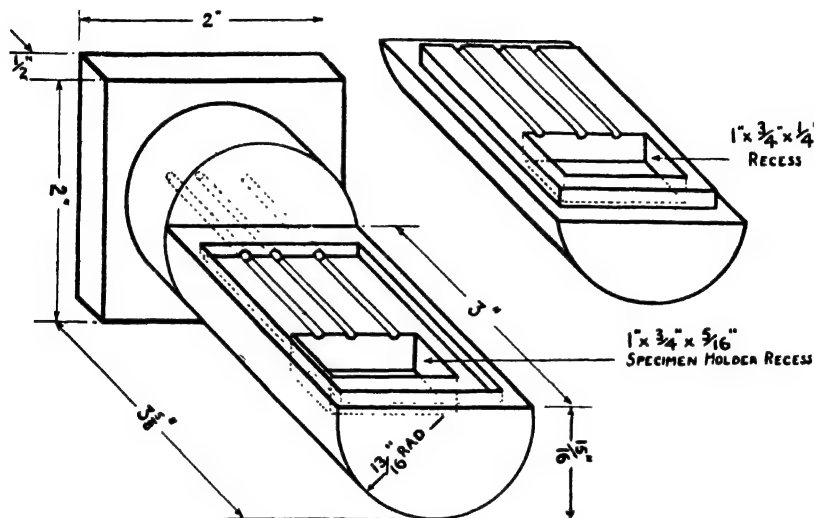


FIG. V.13. DIFFERENTIAL THERMAL ANALYSIS APPARATUS. REFRACTORY BLOCK ASSEMBLY (after Grimshaw and Roberts)

with metal blocks. On the other hand, the rate of rise in temperature is usually more uniform throughout when metal blocks are used, especially at low temperatures. When thermal effects are to be measured which occur below 200°C. , a nickel steel block is preferred.

The furnace design most suitable for the purpose consists of a mullite or similar refractory tube (1.8 in. internal diameter, 0.1 in. wall thickness, and 7 in. long), the central 5.5 in. of which is wound with nichrome wire¹ 0.05 in. in diameter, in such a way that the winding has a total resistance of 11 ohms. The wire is anchored at both ends, coated with a thick slip of alumina or other suitable refractory, dried, and placed in a furnace case 9 in. \times 6 in. \times 9 in., made of sheet metal. The space between the tube and the case may be packed with diatomaceous earth or calcined china clay, but immediately around the tube it is better to have a layer of alumina or sillimanite powder to withstand the high temperatures.

¹ When thermal tests at temperatures higher than 1000°C. are required, a nichrome tape winding will give long life up to about 1200°C. , but for temperatures up to 1300°C. a platinum-wound furnace is essential.

Furnaces constructed in this way are excellent in service and are very durable when used up to 1000° C. There would probably be no disadvantage in using a wire-wound furnace with a higher resistance, although if it is greater than 40 ohms it would not be suitable for tests requiring a controlled rate of temperature rise unless a step-up transformer is also used.

The standard thermal analysis block fits rather loosely into a tube of 1.8 in. diameter, but this is an advantage because it is better to support the block in a refractory ring and thereby prevent direct contact with the furnace tube. Heating is entirely by radiation and troublesome conduction effects are avoided.

The **electric heating current** to the furnace is supplied from a variable transformer. If greater simplicity is desired, a fixed 3:1 step-down transformer may be used, with a heavy-gauged rheostat of about 12 ohms in the primary circuit for control purposes. In the choice of heating rate there is a great divergence of view in the design of thermal analysis equipment. Some investigators prefer to control the input to the furnace to give a heating rate which falls steadily as the temperature is raised; other workers favour a linear rate of rise, which is secured by continuously increasing the electrical input to the furnace. There is little to choose between the two methods, provided that a reproducible rate of rise of temperature can be ensured.

When a controlled electrical input is used no elaborate equipment is necessary, small fluctuations in mains-voltage and change in resistance of the furnace wire can be compensated by manual adjustment of the variable transformer or rheostat. When a furnace of the type described is used, an input of 275–300 watts raises the temperature from 0–1000° C. in 100 minutes. If constant conditions are maintained the heating period required is reproducible to ± 20 seconds.

One disadvantage of the constant input method is that a time against temperature graph has to be plotted, and peaks in the thermal curve related to temperature by reference to this graph. A further disadvantage is that reactions taking place at different temperatures cannot be compared directly because the heating rate is not constant. Such difficulties are overcome, to some extent, by adopting a linear rate of temperature rise. The most usual method is to record the temperature on a potentiometric controller fitted with a cam wheel which is contoured to give the rate of rise required. The electrical input is in two parts; (i) the primary source supplying the furnace directly, and (ii) the secondary current regulated by the controller, so that it boosts the primary current when the rate of heating is too slow, or switches off when the heating-rate is too rapid. In practice, the primary source has to be increased as the temperature is raised, therefore it is necessary to use a variable transformer, with a motorised drive. A heating rate produced in this way is sensibly linear over the complete range of temperature of test, but it is difficult to avoid a step-wise increase which arises as a result of the constantly changing electrical supply. Under these conditions it is almost impossible to reproduce thermal curves quantitatively.

The use of proportional controllers and modern high speed recorders has largely solved the problems, and such instruments are now frequently employed in America; unfortunately, the initial cost of installation of such elaborate equipment is very high.

Another point to be borne in mind is that a linear rate of rise is secured in the inert reference sample only. When endothermic or exothermic reactions take place in the specimen holder, the heating rate cannot be linear, so there is some doubt whether a constant rate of temperature rise is a necessity in the qualitative and quantitative determination of minerals.

Whether the method of constant input or the linear rate of rise method is chosen, a suitable heating rate must be selected to bring out the reactions in the sample to the best advantage. For general work on the minerals in clays, a temperature rise of about 10°C . per minute is most useful, but, it is often advisable to reduce this rate, especially when low temperature effects are of importance or if two minerals are present with closely separated reaction temperatures. The lower the rate of rise of temperature, the less pronounced will be thermal effects from endothermic reactions, but if the rate is too rapid several reactions may be superimposed.

The **methods of recording thermal effects** depend largely on the reactions which occur in the sample. In thermal analysis tests the difference in temperature between the sample and the inert reference material is measured continuously as the temperature is raised. If no reaction is taking place, there will be zero current across the differential thermocouple and no deflection on the galvanometer to which the thermocouple is connected. When a reaction takes place, a difference in temperature between the test sample and the inert material results which creates a net E.M.F. in the thermocouple system, and causes the galvanometer to be deflected. Two opposing effects occur, (i) the heat of reaction tending to increase the temperature difference, and (ii) the restoring influence of the furnace environments. As long as the first effect predominates, the galvanometer will be further deflected from the zero position, but when the reaction rate declines, the sample is restored to the temperature of the inert and the galvanometer returns to zero.

The thermal curve therefore consists of a series of peaks superimposed on a base line. The peaks may be either above or below the base-line, depending on whether the reaction is endo- or exo-thermic, and will have magnitudes in proportion to the heat of reaction.

The galvanometer used for measuring the differential temperature must be sensitive enough to record the effects produced, and yet must have sufficient stability and rapidity of action. When natural clays are being examined, temperature differences of up to 50°C . are developed using 0.8 gm. of material. On the other hand, the minerals in siliceous samples have endothermic reactions which produce temperature differences of only about 2.5°C .

Most of the few commercial recording galvanometers suitable for thermal analysis work need a little modification. The deflection of the galvanometer is recorded either by a continuous pen system or by a chopper bar mechanism. To be suitable for clay mineral studies, a sensitivity of not less than 0.1 millivolts per cm. is required, which, if chromel-alumel thermocouples are used, is equivalent to a temperature difference of 2.5°C . per cm. If the sensitivity of the instrument is too great, a resistance may be included in the galvanometer circuit either in series or as a shunt.

When the thermal effects are very small, a more sensitive system of recording is necessary. One method is to use a D.C. amplifier which magnifies the differential voltage sufficiently to allow it to be recorded on a suitable ammeter or galvanometer. Alternatively, a mirror galvanometer may be used for measuring the differential temperatures. The deflections may be observed on a scale, and visual readings taken at certain time intervals, or the beam of light may be reflected on to photographic paper. Such a recorder has proved of value in the detection and estimation of silica minerals. A beam of light is projected on to the mirror of the galvanometer, from whence it is reflected through a narrow slit in a light-tight container on to a cylindrical drum. Photographic paper encircles the drum which is of 12 cm. diameter and 30 cm. long. The drum is rotated during the test by an electric motor geared to give one complete revolution during the period of test. The rate of temperature rise must be recorded independently on the alternative thermocouple system in order to relate peaks on the thermal curve to the temperature of reaction.

A recent modification has eliminated the need for replotting the thermal effect. The differential thermocouples are taken as usual to the mirror galvanometer, but the couple measuring the direct temperature (*b, c* in Fig. V.12) is connected to a recording potentiometer. As the temperature of the furnace increases, the potentiometer is made to drive the drum of the photographic recorder through a gearing mechanism to the driving wheel. Thus, the thermogram on the photographic paper is a trace of the differential temperature against the actual temperature of the inert material.

The *advantages of differential thermal analysis* lie in its relative simplicity and the rapidity with which results may be obtained. Furthermore, certain minerals can be identified (and often the amount of each may be estimated) even when they are present in complex mixtures. The method is of particular value in the analysis of clays, for the principal impurity, quartz, has only a small endothermic effect which does not interfere with the peak of the clay minerals. Moreover, the endothermic change in quartz is reversible with temperature, whilst that in clay minerals is not. Thermal tests on calcined clay using a sensitive method of recording will indicate the presence of quartz.

One difficulty which is encountered in thermal analysis is the variability of results obtained from one apparatus to another. This has now been virtually overcome by using a widely-accepted design, but even then slight fluctuations in the heating rate of the furnace may introduce errors. Other factors which need strict attention if good reproducibility of results is to be attained are the position of the thermocouple junctions and the packing density of both the test-sample and the reference material.

If these requirements are observed, the reproducibility of results is generally good, although when using pure minerals which exhibit large thermal effects (e.g. kaolinite), considerable deviations may be found between duplicate experiments and may call for multiple determinations to obtain reliable results.

The principal difficulty encountered in differential thermal analysis is that appreciable temperature differences may occur during the test which are not due to the evolution or absorption of heat in the test-sample. As a result, the zero or base-line deviates from the horizontal. This 'drift' can be caused by:

(i) Unsymmetrical location of the sample-container in the block, or of the block itself in the furnace. These are constructional faults and easily corrected.

(ii) Poor fit between the lid and lower half of the block causing localised overheating. This may be overcome by fitting the lid with a tongue which engages in a groove in the lower half of the block (cf. Fig. V.13).

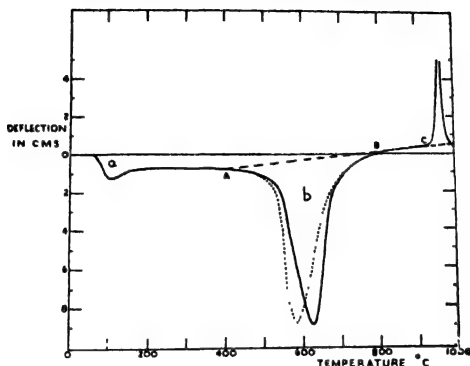


FIG. V.14. DIFFERENTIAL THERMAL CURVE SHOWING BASE LINE CORRECTION

There is a third cause of drift which is more difficult to eliminate. Since thermal analyses are conducted on a rising-temperature basis, the rate of temperature rise in both the test and reference materials depends on their respective coefficients of thermal diffusivity. Not only may these be different at the start, but both will vary as the temperature is raised and not necessarily at the same rate. In addition, the thermal diffusivity of the test material may alter considerably when the mineral decomposes.

The drift of base-line from this cause may be greatly reduced by choosing a reference material with thermal characteristics approaching those of the test-sample as closely as possible, and it is usually advisable to use precalcined test-material for this purpose. The recorded curves are then corrected for the remaining drift in the following manner.

In Fig. V.14 is shown a typical thermal curve (for kaolinite) in which the temperature difference between the test-sample and the inert material is plotted as ordinate, and the temperature of the inert material as abscissa. After the endothermic effect corresponding to decomposition of the mineral has occurred, the *drift* is regular and progressive so that the observed base-line (B-C) is straight and slightly inclined to the horizontal; this effect is found in almost every case. The line BC is then projected back to A, the point at which the exothermic reaction begins; the peak height and area are then measured relative to ABC and the curve replotted with ABC as the base-line. This procedure is admittedly arbitrary, but appears to be justified by the increased reproducibility of results which it frequently secures.

To attempt to catalogue all the refinements and modifications to the apparatus used in differential thermal analysis by the many workers in the field would be

impossible.¹ Units range from the simplest, costing a few pounds and occupying little space, to the most complex, comprising the latest electronic devices and requiring most of the space in a large room for housing. It is debatable whether the latter has the advantage that the extra cost would suggest. Of prime importance is that the operator should appreciate the limitation of the method and his own apparatus in particular and design his experiments accordingly.

The apparatus described in the previous pages represents a basic type of comparatively low cost, but nevertheless one which has proved eminently satisfactory for most applications of differential thermal analysis, with, at the most, minor refinements.

APPLICATIONS OF DIFFERENTIAL THERMAL ANALYSIS

THIS method of analysis has several important applications of which the chief are:

- (i) The identification of minerals.
- (ii) The estimation of the content of some minerals in composite mixtures.
- (iii) Assessing the principal reactions and the temperatures at which they occur in ceramic bodies on firing.

The identification of minerals by differential thermal analysis is based mainly on observations of the temperature of the *peaks* (maximum or minimum) of the thermal curve. The temperatures plotted on the horizontal axis of the observed curve are those of the inert material.² It is important to note that the 'peak' temperature derived in this way does not indicate the true temperature of the test-sample, which is lower or higher than that of the inert material because of the endothermic and exothermic reactions. For this reason, the peak temperature, when so measured, is affected by the amount of mineral in the sample but if the observed curve is redrawn and plotted against the *true* temperature of the test-sample, the temperatures corresponding to the peak of the curve are, on the whole, almost independent of the amount of mineral in the sample.

In endothermic reactions, the *true temperature* is obtained by subtracting the observed differential temperature from the corresponding temperature of the inert material, whilst the latter is used to compute the temperature-time (rate of heating) curve.

The sharp distinction secured by thermal analysis between minerals of the kaolin group and the montmorillonites is shown by typical curves for kaolinite (A) and montmorillonite (C) in Fig. V.15. The curves illustrated here are those obtained with 'diluted' test-samples which contained only 50 per cent of the mineral, the remaining 50 per cent being calcined material.

Kaolinite is characterised by a relatively large endothermic effect (maximum at approximately 585° C.), which corresponds to the well-established breakdown of the crystal lattice in this temperature range. The sudden and pronounced exothermic reaction at 980° C. is also characteristic of the kaolin-group minerals.

¹ For fuller details see *The Differential Thermal Investigation of Clays*, edited by R. C. Mackenzie, Mineralogical Society, London, 1957.

² In American practice the temperature of the metal block is frequently used

The endothermic effect in *montmorillonite* (b, curve C) is much less pronounced and occurs at higher temperatures (maximum at 700° C.); an exothermic change (c) is also noticeable, but takes place at a lower temperature than with kaolinite and, in addition, is preceded by a small endothermic effect (d).

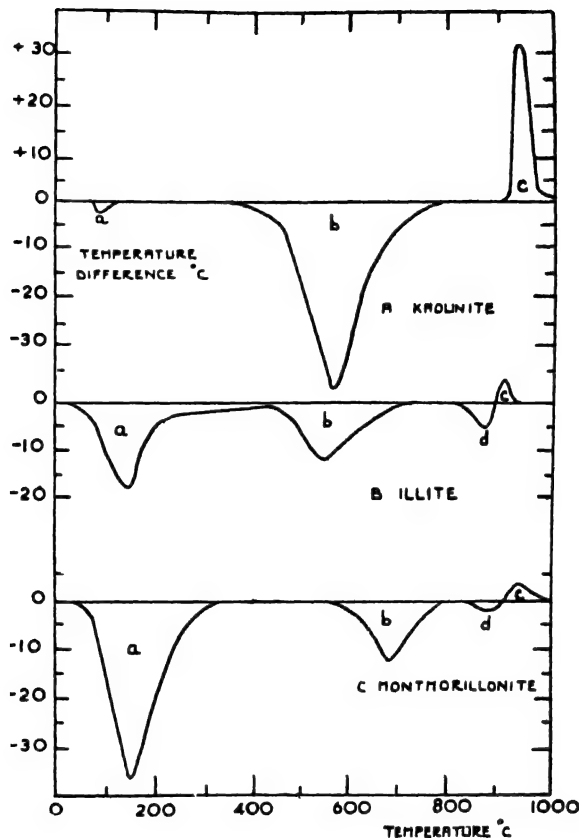


FIG. V.15. DIFFERENTIAL THERMAL CURVES OF
(A) KAOLINITE; (B) ILLITE; (C) MONTMORILLONITE

Illite gives a relatively small thermal effect, occurring very nearly at the same temperature as that of kaolinite. The curve B in Fig. V.15 is of the mineral from Fithian shales described by Grim.¹ Hydrous micas from British clays have a rather different thermal curve which is shown in Fig. V. 16 along with curves of typical fire-clays.

Fig. V.17 shows curves obtained with laboratory-made mixtures of *montmorillonite* and *kaolinite*. With the technique used in the general examination of clays,

¹ Grim, R. E., *J. Amer. Ceram. Soc.*, 27, 65, 1944.

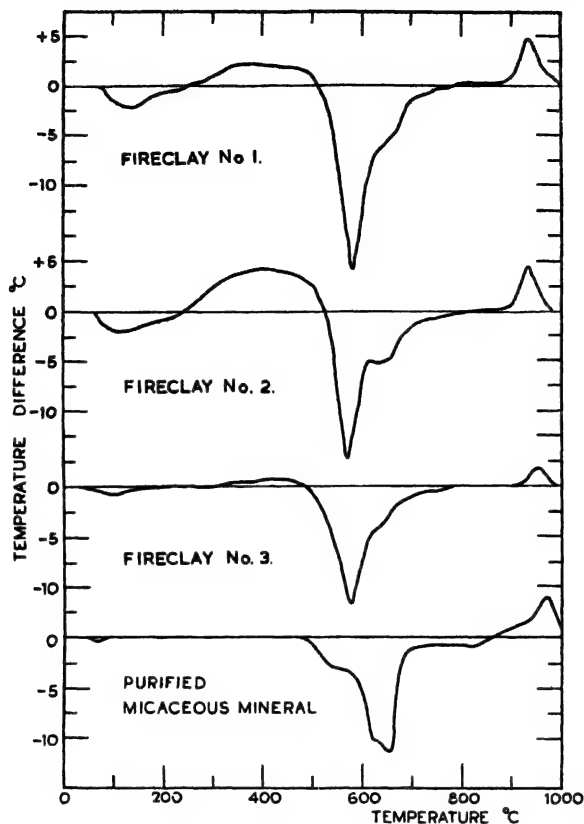


FIG. V.16. DIFFERENTIAL THERMAL CURVES OF BRITISH FIRECLAYS AND THE MICACEOUS MINERAL SEPARATED FROM THEM

about 5 per cent of montmorillonite can be detected with certainty, and amounts down to approximately 2 per cent can be observed by increasing the sensitivity of the temperature recorder.

A number of the accessory minerals in *refractory clays* can be detected by thermal effects which correspond to the loss of combined water or carbon dioxide on heating. Thus, *trihydrate of alumina* gives an exceptionally large peak at 305° C., followed by a further endothermic effect at 520° C. The *monohydrate* is characterised by a pronounced single peak at 550° C. The relationship between the hydrates of alumina presents a special problem which is still under investigation.

Iron-bearing minerals of importance as constituents of clays include the hydroxide *goethite* (FeO.OH) which gives an endothermic effect at about 350° C., *iron pyrite* (FeS_2) is characterised by an exothermic at 450° C., whilst the presence of *ferrous carbonate* (FeCO_3) can also be established by thermal analysis. Other

carbonates which can be detected in amounts of 2 per cent and upwards include *calcium carbonate* (CaCO_3) and *magnesium carbonate* (MgCO_3). A thermal curve for *dolomite* is included in Fig. V.18 to indicate the possible application of thermal methods to the analysis or control of dolomitic raw materials; the areas *c* and *d* correspond to the decomposition of magnesium and calcium carbonates respectively.

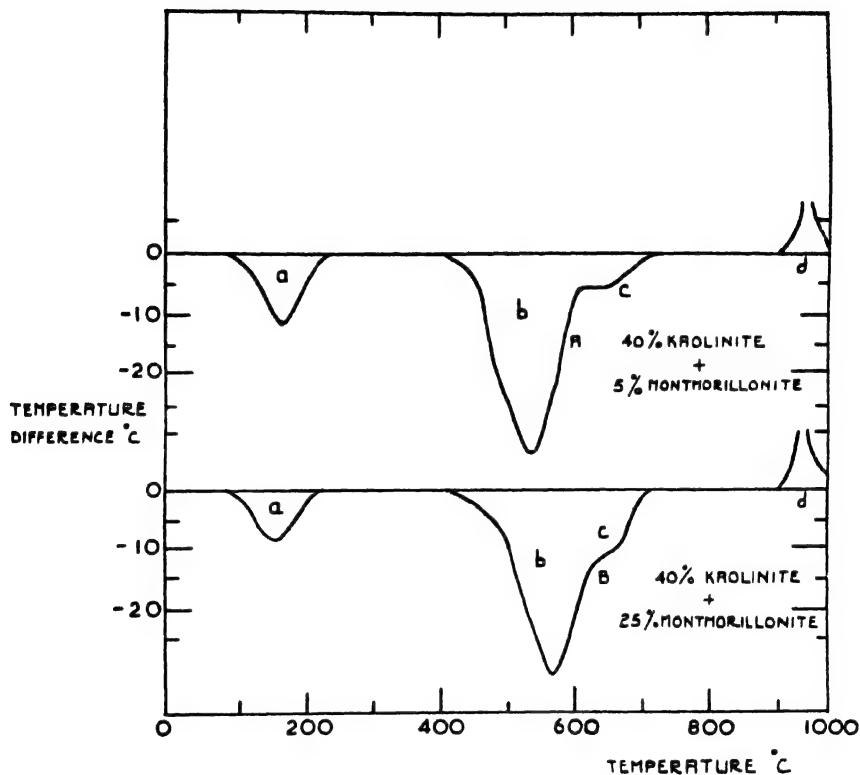


FIG. V.17. DIFFERENTIAL THERMAL CURVES OF MIXTURES OF KAOLINITE AND MONTMORILLONITE

Carbonaceous matter gives rise to exothermic effects over a wide temperature range; they are often so pronounced as to reduce or even obliterate any endothermic changes which may take place simultaneously.

When subjected to thermal analysis, clays in the air-dried condition usually show an endothermic effect with its peak at about 100°C ., corresponding to the evolution of hygroscopic water. Peaks with maxima at higher temperatures (e.g. 150°C .) are also common, and indicate the presence of water molecules in stronger association with the clay. These peaks persist in clay samples which have been oven-dried at $105\text{--}110^{\circ}\text{C}$., whereas the 100°C . peaks are removed.

Differentiation between the kaolin minerals themselves is quite easy by thermal analysis. In fact, the mineral *livesite* was first recognised in fireclays and allied materials by thermal tests.¹ Figs. V.19 a and b show the curves for the various minerals of the kaolin group.

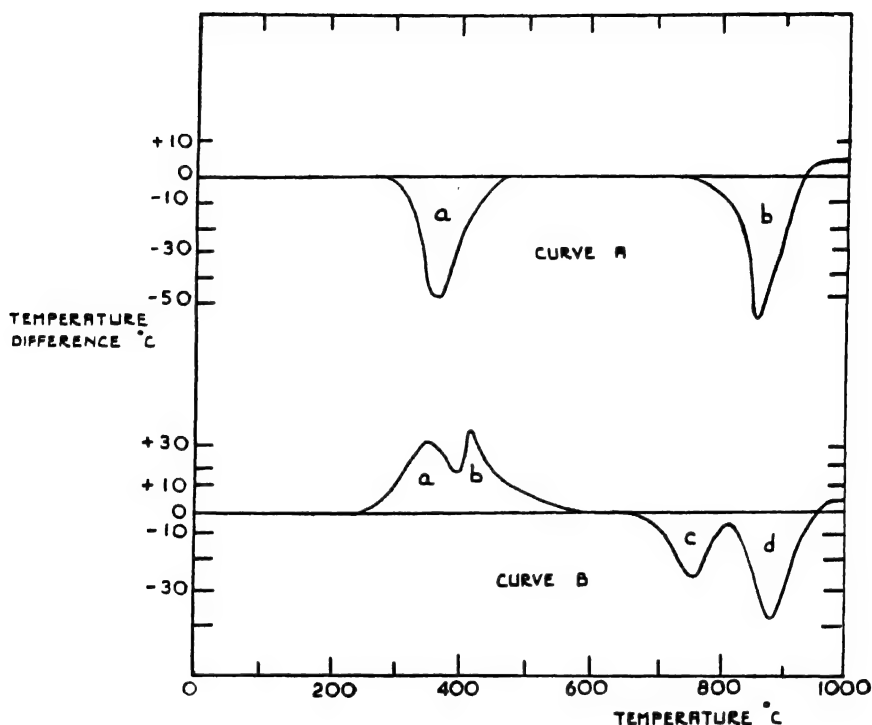


FIG. V.18. DIFFERENTIAL THERMAL CURVES OF (a) A FERRUGINOUS LIMESTONE AND (b) A DOLOMITE CONTAINING CARBONACEOUS MATTER

Many other minerals may be identified and there are numerous references in the literature. Special mention may be made of the analysis by thermal methods of *basic raw materials*,² and the *serpentine minerals*,³ which are of importance as ceramic raw materials.

The characteristic peaks of many of the minerals identified by differential thermal analysis which have been compiled by R. W. Grimshaw and his colleagues, using the apparatus described in the previous pages, are given in the Appendix.

From the description given above, it will be noted that the method is applicable

¹ Grimshaw, R. W., Heaton, E. and Roberts, A. L., *Trans. Brit. Ceram. Soc.*, **44**, 69, 1945.

² Howie, T. W. and Lakin, J. R., *Trans. Brit. Ceram. Soc.*, **46**, 12, 1947.

³ Shorter, A. J., *ibid.*, **45**, 340, 1946.

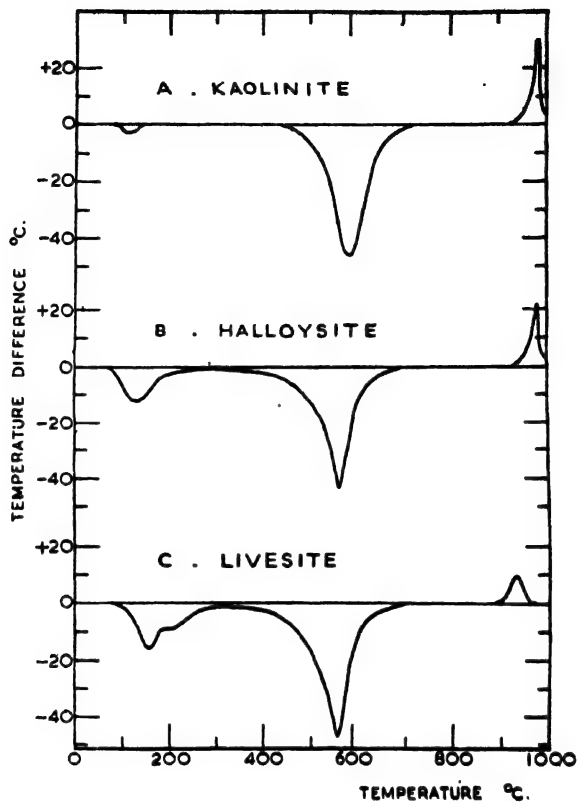


FIG. V.19(a). DIFFERENTIAL THERMAL CURVES OF THE KAOLIN MINERALS

to the principal clay minerals and to most of the accessory components, with the notable exception of alkali-bearing constituents such as *micas* (other than the hydrous *micas* or *illites*) and *felspars*, which appear to be thermally inert.¹

The *silica minerals* are also capable of identification by thermal means,² but because the thermal changes which take place are the result of the reversible inversions with a small heat change (see p. 617), a sensitive method of recording is essential.

The Quantitative Determination of Minerals by Differential Thermal Analysis. The peaks in differential thermal analysis are the direct result of the heat change during a reaction. Because this heat change corresponds to the energy of

¹ Köhler, A. and Weiden, P. (*Neues. Jb. Miner. Mh.* 249, 1954) have suggested that some *felspars* invert to high temperature varieties in the temperature range 700–900° C., and that such changes are accompanied by a thermal effect of small magnitude.

² Grimshaw, R. W., Westerman, A. and Roberts, A. L., *ibid.*, 48, 269, 1948.

reaction, it can be predicted theoretically that the area under a characteristic peak of a mineral is related to the energy change during the reaction; hence if that reaction is specific in both magnitude and temperature to all samples of the mineral, the amount of the mineral present in a composite sample will be related to the peak area.

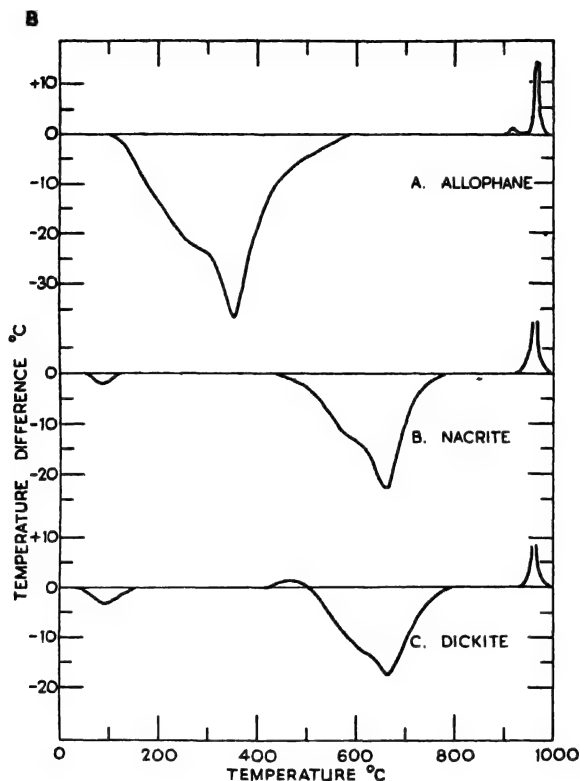


FIG. V.19(b). DIFFERENTIAL THERMAL CURVES OF THE KAOLIN MINERALS

The first and prime essential for the quantitative estimation of minerals by differential thermal analysis is that the technique for carrying out the tests should be rigorously standardised; only under these conditions are accurate measurements possible.

Thermal analysis measurements are relative in that conclusions can be drawn only by comparing the curves of an unknown sample with those of known materials. So, with quantitative measurements, the thermal curves of different proportions of pure minerals are required for an analysis. To be capable of estimation, minerals must give well-defined thermal curves with at least one peak sufficiently distinctive and capable of accurate measurement, e.g. the kaolinite decomposition peak at

590° C. The peak corresponding to the loss of hygroscopic water would not be suitable for quantitative work, nor would a peak which is liable to interference by commonly associated impurities, e.g. the exothermic peak in kaolin minerals at 980° C., which is modified or suppressed by certain soluble salts particularly sodium sulphate.

Grimshaw and Roberts¹ have shown the value of the method for the quantitative determination of some ceramic minerals and have demonstrated the limits of accuracy. They point out that the main source of error in such measurements is due to differences in thermal characteristics (specific heat, thermal diffusivity, etc.) between the test-sample and inert reference material. It can be eliminated or largely reduced by diluting the test-sample to 25 per cent with the inert material and increasing the sensitivity of the recording equipment.

Under these conditions, kaolinite, halloysite, montmorillonite, calcium carbonate and many other minerals can be measured under favourable conditions with an accuracy of ± 1 per cent.

One difficulty encountered in the estimation of minerals, not only by thermal analysis, but by all other methods, is the isolation of a pure mineral sample which is representative of that mineral wherever it is found. Some minerals present no difficulty; calcite, for example, occurs in a pure state in nature and apparently has a similar thermal effect in all cases. Kaolinite also is well-defined and can be purified from crude china clay by centrifugal separation. Other kaolin minerals may be inter-mixed and difficult to isolate; however the characteristic endothermic peaks at about 550–600° C. of kaolinite, livesite and halloysite are all of similar magnitude so that the total content of kaolin minerals in a mixture can be estimated, even though the individual proportions cannot be ascertained. Other minerals, such as the montmorillonites are variable in composition (see p. 148), and their estimation by thermal means should always be undertaken with caution. In any one particular deposit an 'average mineral' may be obtained by suitable methods of purification, and differential thermal analysis may then be used to estimate the content of that mineral in other samples from the same deposit.

The *silica* minerals present many anomalies in their detection and estimation by differential thermal analysis.

Quartz may be identified by the heat change of its inversion at 573° C. Usually this change is rapid and reversible and for a variety of reasons it is better to measure the change on the cooling cycle,² recording the thermal effects by a sensitive mirror galvanometer. For most samples of quartz the maximum of the differential peak occurs at the same temperature and the form of the curve is similar. Keith and Tuttle³ have demonstrated that in exceptional cases, quartz can show an anomalous inversion and in many instances, a particular sample may invert over a range of temperature (amounting to 2–3° C.) rather than at one definite point. However, the analysis of many quartz samples by normal differential thermal methods has shown that the peak area is virtually constant in amount and independent of the sample. The method of using peak height as a basis of mineral content, whilst satisfactory

¹ Grimshaw, R. W. and Roberts, A. L., *Trans. Brit. Ceram. Soc.*, **52**, 50, 1953.

² Grimshaw, R. W., Westerman, A. and Roberts, A. L., loc. cit., 1948.

³ Keith, M. L. and Tuttle, O., *Amer. J. Sci.*, **1**, 203, 1952.

for well-crystalline quartzites, is less accurate than area measurements when the quartz is in the form of fine crystallites.

Both *cristobalite* and *tridymite* invert at a low temperature, hence the method of cooling as in quartz cannot be used without considerable modification to the apparatus. The changes are therefore best measured on the heating cycle, but with a reduced rate of rise (6–8° C. per min.) than that normally employed. Less drift is encountered if a metal block is used instead of the usual refractory one, although the thermal peaks are reduced as a consequence.

The inversion temperature of *cristobalite* varies between 224–269° C.; it appears to depend on the temperature at which the cristobalite is prepared and on the type of catalytic agent. Differential thermal curves of cristobalite samples from different sources show this variability of inversional temperature, and further indicate that the shape of the peak is not identical in all samples.

Despite these differences, the peak area of pure cristobalite is reasonably constant and is independent of the maximum temperature and shape.

Tridymite also provides a complication. Although every sample of this mineral so far tested gives thermal peaks at 117° C. and 163° C., the ratios of the heights of these peaks show considerable variation. The time and temperature of firing and the nature of the fluxing oxide both influence the form of curve. Two forms of tridymite probably exist, one with an inversion at 117° C., and the other at 163° C., and not one form with two inversions.

It has been shown by Gaskell and Grimshaw that the combined areas of the two inversional peaks of the thermal curve of tridymite give a good measure of the content of that mineral in a sample.

Carbonaceous Matter is a common constituent of clays and shales and under oxidising conditions it burns off between 250–600° C. giving a pronounced exothermic peak in a differential thermal analysis test. As such, it is the most serious deterrent to mineralogical identification by this means.

The best solution to this problem is to carry out differential thermal analyses of carbonaceous clays in an atmosphere of nitrogen. The oxidation of the organic matter is thus suppressed and the thermal effects recorded are those of the inorganic minerals. This technique is applicable to estimating some of the inorganic constituents of coals, but if the ash content is less than about 10 per cent, the peaks of distillation and pyrolysis reactions of the coal minerals themselves tend to predominate.

Differential thermal analysis can also be applied to assessing the nature and amounts of carbonaceous material in clays and also to determining the rank and approximate calorific value of fuels.

Influence of Grain Size on Thermal Analysis. Provided that the mineral is not crystallographically distorted or altered as the grain size is reduced, the differential thermal curve does not appear to be seriously influenced by the sizes of the particles in the sample. The thermal curves of many minerals are however, seriously affected by grinding. Many aluminosilicates conform to a general pattern and give results which are remarkably similar. Short-term grinding invariably gives rise to a product with an endothermic peak at about 550° C. when tested by thermal means. In addition, the peak resulting from the loss of hygroscopic water is prolonged and

accentuated and may persist up to 300° C. As the grinding is continued, the endothermic effect at 550° C. increases to a maximum and then declines, whilst the lower temperature peaks increase in size continuously. The probable explanation is that mechanical breakdown occurs by the fracture of corners of crystals, thereby exposing free valencies. Water molecules are absorbed which are held more firmly than hygroscopic water. It is of interest to record that more alumina and silica may be extracted from a ground sample by moderate leaching with dilute acid or alkali than from the original material.

When preparing a mineral sample for thermal analysis, it is therefore advisable to minimise grinding whenever there is a possibility of it causing any breakdown of the mineral.

DOUBLE DIFFERENTIAL TECHNIQUE

NATURAL raw materials occasionally give thermal curves containing several peaks, some of which may mutually interfere. When a composite thermal curve containing two or more clay mineral peaks is obtained by the usual method of testing, it is often possible to decide upon the identity of at least one of the minerals, and to estimate its amount approximately. The test may be repeated, after adding to the inert material the appropriate amount of the mineral already identified in the test-sample. Thermal effects due to this particular constituent thus occur in both the test-sample and in the reference material, and so almost or completely cancel each other out if the correct amount has been added to the latter. By successive approximations it is possible to obtain a thermal curve showing only the thermal effect due to the second mineral. This method is illustrated by Fig. V.20, in which curve A relates to a laboratory-prepared mixture of 40 per cent of kaolinite and 25 per cent of montmorillonite when tested in the usual way against an inert reference material. In this particular instance there is no difficulty in recognising the presence of both kaolinite and montmorillonite, but mutual interference between the two peaks is sufficient to make quantitative interpretation uncertain. Curve B shows the results obtained by repeating the test against a reference material containing 40 per cent of raw kaolinite the rest being pre-calcined material; the principal peak due to kaolinite is almost completely suppressed, and only the montmorillonite peak remains as a major effect. In this case, the sensitivity of the equipment was increased in order to magnify the montmorillonite peak area. The residual kaolinite effect corresponds to an apparent excess of less than 1 per cent of this mineral.

This technique has been termed *double-differential thermal analysis*, and is of great practical value. One particular application which deserves special mention is the determination of small amounts of kaolin clay minerals in ganister and silica rocks. Usually less than 3 per cent of clay is present in such minerals, and consequently the endothermic $\alpha \rightleftharpoons \beta$ inversion of quartz, which occurs at a similar temperature to the breakdown of the clay, is superimposed and prevents accurate measurement. The percentage of quartz may be found by testing a sample of pre-calcined material; this amount of pure quartz may then be included in the standard reference material. The resulting thermal curve of the ganister tested against the new reference is that of the clay mineral alone.

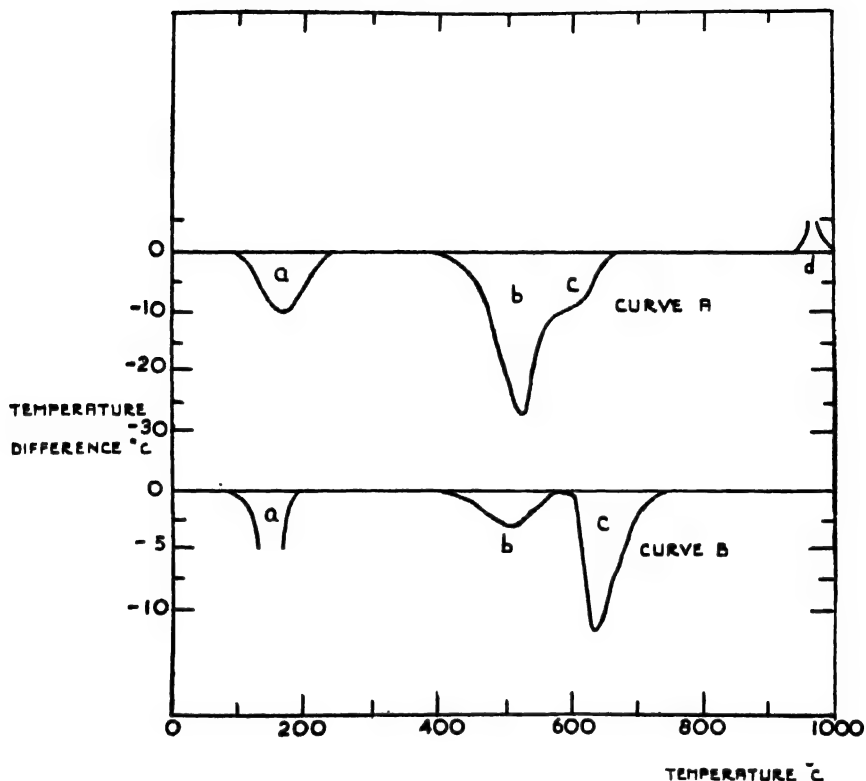
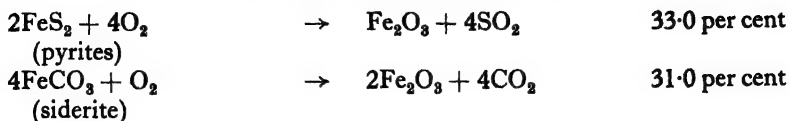


FIG. V.20. DOUBLE DIFFERENTIAL THERMAL ANALYSIS CURVES

WEIGHT LOSS MEASUREMENTS

AS an alternative to thermal analysis methods, which rely on the heat effects, the change in weight when a reaction takes place, may be measured. Weight loss measurements are more limited, and applicable only to those reactions which involve an evolution, or in some cases, absorption, of a gaseous component. They are valuable in clay studies, for many of the principal minerals decompose on heating with the evolution of water or carbon dioxide. Some examples are:

		<i>Loss of weight</i>
$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ (kaolin)	$\text{Al}_2\text{O}_3 + 2\text{SiO}_2 + 2\text{H}_2\text{O}$	13.9 per cent
$\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$ (ideal montmorillonite)	$\text{Al}_2\text{O}_3 + 4\text{SiO}_2 + \text{H}_2\text{O}$	5.06 per cent
CaCO_3 (calcium carbonate)	$\text{CaO} + \text{CO}_2$	44.0 per cent



The reactions take place at well-defined temperatures and, as with thermal tests, a series of standard curves may be drawn up which help in the identification and estimation of many minerals.

The **loss on ignition** at a temperature of about 900° C. is regarded as an important characteristic of many clays. In addition to being a vital determination in the routine chemical analysis of ceramic materials, the total weight loss on calcining is also used as a means of identifying some minerals and as a rough means of estimating the percentage of some of them in various samples. Thus in a sandy clay, in which the clay mineral is almost entirely kaolinitic, the loss on ignition gives a good measure of the clay content. (The weight loss of the pure clay mineral is 13.9 per cent, so if 6.95 per cent loss were measured, the sample would contain half its weight of clay). The type of clay mineral in an unknown sample can often be conjectured if the loss on ignition is determined. It is important to determine the loss on ignition on a sample which has previously been oven-dried, because, otherwise, hygroscopic or absorbed water would contribute to the total.

The loss of moisture, i.e. the loss in weight after drying at 120° C., can itself be an important and an informative determination. Some minerals take up large quantities of moisture on being exposed to the atmosphere; montmorillonites, for example, absorb up to 20 per cent, whilst kaolinite rarely holds more than 2 per cent. Livesite, the kaolin mineral in many sedimentary clays loses about 8 per cent at 120° C. provided that it has been allowed to hydrate fully before testing.

The total weight loss of a sample includes:

- (i) loss of hygroscopic and adsorbed water;
- (ii) loss of colloidal water;
- (iii) loss of water of hydration and absorbed water.

These three are, for the most part, removed by heating to 120° C. for long periods and are usually classified as the loss of moisture.

- (iv) loss of combined water, which is part of the structure of minerals;
- (v) loss of carbon dioxide or monoxide from the burning of carbonaceous material or the decomposition of carbonates;
- (vi) loss of sulphur dioxide and trioxide from sulphur compounds, such as pyrites, sulphates, etc. In exceptional circumstances, hydrogen sulphide, H_2S , may sometimes be evolved;
- (vii) loss of various other gases and volatile substances present in the material.

For an accurate and complete analysis, the individual proportions of water, carbon dioxide and sulphur dioxide liberated should be estimated separately.

Although it is usual to determine the total loss on ignition by heating at a high temperature (above that at which all the minerals will decompose) much information can be obtained from tests in which the sample is raised in temperature at an extremely slow rate and weighed at several temperatures. Such tests can be

extremely tedious, especially if the sample is allowed to reach equilibrium at each temperature; for example, a kaolinite sample reached a sensibly constant weight only after two months at 410° C., and even then there was a small yet appreciable weight loss at slightly higher temperatures!

Excellent differentiation between different minerals may be secured by such careful measurements. Livesite, for example, loses almost all its combined water at 405° C., kaolinite reacts at 410° and halloysite at 400° C. Montmorillonites, micas and other minerals can be identified in a similar way.

A neat method of recording the *rate of weight loss* in a sample has been described.¹ Reactions involving an evolution of a gas give peaks with a maximum which corresponds to the temperature at which the reaction is proceeding at its fastest rate. The form of typical curves for clays obtained from this apparatus are not unlike those from differential thermal analysis, except that there is no differentiation between endo- and exothermic effects.

REHYDRATION METHODS

THE property of *adsorbing* and *absorbing* water from the atmosphere is possessed by all clay minerals to a greater or less extent, the amount being determined by (a) the surface area of the material, and (b) its chemical and physical nature. For example, montmorillonite, which has a much smaller grain size, and hence a larger specific surface area than kaolinite, adsorbs much more water; but when saturated with various bases it will absorb different amounts of water depending upon the ease of hydration of the cations.

In the kaolinite group, where little ionic effect can be expected, water will be adsorbed only and the amount of adsorption will depend on the relative surface area of each mineral.

A simple rehydrator can be constructed from a desiccator with water substituted for the drying agent. Small petri dishes containing the sample of clay dried at 250° C. are placed in the rehydrator and weighed from time to time. The test is best carried out at constant temperature in order to standardise humidity conditions.

Berkelhamer² has stated that it is necessary to dry the samples at temperatures of about 250° C. to eliminate all absorbed water which in the case of montmorillonite may not be released much below 200° C.

Results obtained on samples of kaolinite, halloysite, montmorillonite (Wyoming) and a foundry bond clay rich in livesite are shown in Fig. V.21. Although the test is not sufficiently critical to be diagnostic of a particular mineral, it does indicate the mineral type, and is also of value in assessing the behaviour of a clay under atmospheric conditions.

BASE EXCHANGE CAPACITY

ALL clay minerals adsorb positive cations by virtue of the unsaturated negative ions in the surface layers. In addition, montmorillonites, and to a lesser extent some

¹ Bird, R. T. H., *Claycraft*, 30, 340, 1957.

² Berkelhamer, L. H., *J. Amer. Ceram. Soc.*, 26, 130, 1943.

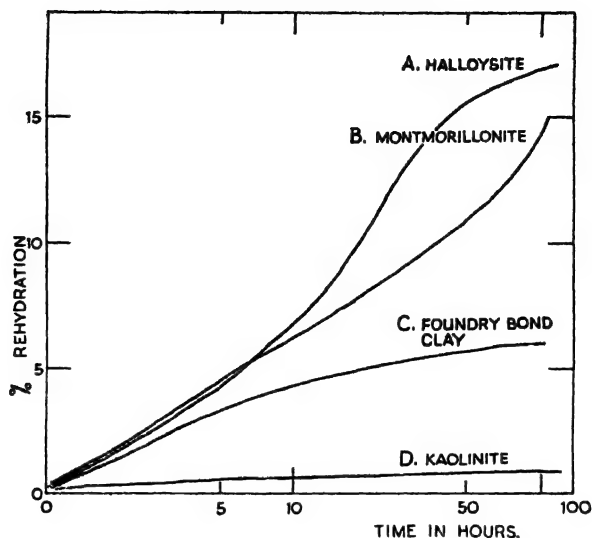


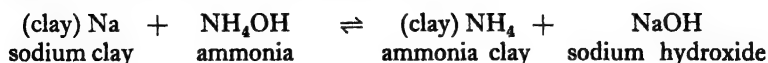
FIG. V.21. THE RATE OF REHYDRATION OF SOME CLAYS

finely grained illites absorb cations because they have a charge deficiency within the lattice. These cations are held by only feeble electrical forces and are easily replaceable by others.

That soils were able to remove ammonia from aqueous solution was first recognised by J. T. Way, who reported his finding to the Royal Agricultural Society in 1850 and 1852. The absorption of bases in this way does not involve any structural change in the minerals, and as one base is taken up from solution, another is generally released in its place. Hence this property of soils and clays became known as the *base exchange capacity* (b.e.c.).

Physical chemists now recognise that the exchange is between cations, e.g. an ammonium ion (NH_4^+) will replace a sodium ion (Na^+), so that it is more correct to refer to the property as being the *cation exchange capacity* (c.e.c.).

It is not unusual for a natural clay to absorb several cations. The common ones are hydrogen (H^+), sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}) and aluminium (Al^{3+}). It is customary to distinguish between clays in which one cation is predominantly or exclusively absorbed; thus a sodium clay is one in which the absorbed cation is sodium. The exchange reaction between two cations associated with a clay may be expressed as follows:



One equivalent weight of ammonium replaces an equivalent weight of sodium, hence it is customary to measure the cation exchange capacity in terms of milliequivalents (i.e. a thousandth of an equivalent) of oxide per 100 gm. of clay.

The method of calculation for a sodium clay is as follows: The molecular weight of Na_2O is 62 (i.e. $2 \times 23 + 16$); this contains two atoms of Na, hence the equivalent weight of Na_2O is $62 \div 2$, i.e. 31. One milliequivalent of Na_2O therefore corresponds to 0.031 gm. Na_2O , and if this quantity were associated with 100 gm. of clay, then the *cation exchange capacity* would be 1 milliequivalent per 100 gm.

The cation exchange capacity of clays is known to have a pronounced influence on their properties (see Chapter VIII). The fertility of soils is partially dependent on the inorganic salts held in this way. In addition, a measurement of the cation exchange capacity may provide useful information to the ceramist as to the nature of the minerals in a clay. It may be determined by (i) electrodialysis, or (ii) by a chemical method.

In electrodialysis a cell is used which consists of three compartments, the two end ones being separated from the centre by a semi-permeable membrane or a suitable porous plate. The end compartments are filled with distilled water and in the centre one is placed a known weight of the sample, suspended in distilled water. A direct electrical potential (100 volts) is applied between platinum electrodes in the two end cells and this causes the cations absorbed on the clay to migrate through the membrane to the negative electrode. After a period of time, when the test is judged to be completed, the alkalinity of the solution in the cell containing the negative electrode may be measured by titration with a standard solution of acid. From this, the total cation exchange capacity (other than hydrogen ions) can be calculated. If it is required to know the types of cations associated with a clay, a quantitative analysis must be carried out on the solution.

The chief effect in electrodialysis is to replace the exchangeable cations by hydrogen cations, but it is alleged that some clay minerals, montmorillonites in particular, tend to be broken down and release cations which are normally part of their structure. Some iron compounds may also be removed by this treatment.

In the chemical methods, the sample is treated with a cation which readily replaces all others and at the same time is capable of easy estimation. Ammonium (NH_4^+) is probably the most convenient ion to estimate, but it is not absorbed by clays in preference to such ions as calcium, magnesium or hydrogen. However, if a salt of ammonia is used, the anion of which forms an insoluble compound with most other ions, quantitative replacement can be effected. Ammonium acetate is most commonly employed, because not only are the acetates of calcium, magnesium, etc., insoluble, but any hydrogen ion is removed as undissociated acetic acid.

The usual procedure is to treat a known weight of the sample with a normal (1.0N) solution of ammonium acetate. Five or six such treatments are normally required to ensure complete replacement and between each, the samples should be allowed to sediment and the clear liquid decanted. If a centrifuge is available, this stage of the determination can be completed rapidly. Excess ammonium acetate is removed following the final treatment by washing with alcohol.

The sample is then transferred to a long-necked (Kjeldahl) flask, an excess of sodium hydroxide added and the ammonia distilled off—preferably on a steam bath—and collected in a known volume of standard (N/10) sulphuric acid. When the distillation is complete, the ammonia which has been liberated is estimated by back-titrating the remaining acid with a standard solution of alkali. Further details

of the method have been published by Truog¹ and a useful micro-method has been described by Mackenzie.²

In many cases, the type and amount of the cations associated with a particular clay in its natural state are equal to or greater in importance than the total exchange capacity. For the most part, these can be identified and estimated by carrying out a standard analysis on the decanted liquids which are collected after each washing with ammonium acetate. Exchangeable hydrogen is best estimated on a separate sample, using barium acetate³ which replaces hydrogen more rapidly and completely than does ammonium acetate. The free acetic acid which forms can be titrated against a standard solution of alkali (NaOH), with phenol-phthalein as an indicator.

TABLE V—IV. THE CATION EXCHANGE CAPACITIES OF CLAYS

Clay mineral	Total cation exchange capacity (m.e./100g.)	Cations originally present				
		Ca	Mg	Na	K	H
Kaolinite (china clay)	5.74	3.12	0.61	0.41	0.40	1.20
Halloysite (Eureka)	12.76	0.50	1.25	1.74	1.56	7.71
Livesite (from bond clay)	39.3	—	—	—	—	—
Montmorillonite (Wyoming)	76.46	17.72	14.78	38.75	3.31	1.90
Hydrous Mica (from fireclay)	4.50 (variable)	0.00	0.00	0.62	3.43	0.45
<i>Natural Clays</i>						
Ball Clay (Dorset)	14.45	4.62	0.32	5.23	0.31	4.00
Bond Clay	21.5	—	—	—	—	—
Fireclay (weathered)	10.65	1.75	3.70	0.68	0.84	3.68
Fireclay (unweathered)	11.32	7.45	1.72	0.81	0.54	0.80
Brick Clay (Jurassic bed)	7.32	3.62	2.26	0.05	0.02	1.37
Bentonite	56.80	18.86	2.55	28.04	3.89	3.46

Other methods of determining the cation exchange capacity of clays have been described, but none is of such general application as those outlined.

In a rapid method of determining the cation exchange capacity devised by Robertson and Ward,⁴ a known volume of a standard solution of methylene blue is shaken up with a weighed quantity of the sample which is suspended in water. After several hours, an aliquot part of the clear liquid is withdrawn and the colour compared with other samples of the dye solution diluted with known quantities of water. From this comparison, the amount of colour adsorbed by the sample can be calculated. This method is particularly useful for industrial tests, but it is not as accurate as the ammonium acetate technique. The type of ion associated with the clay may affect the colour of the methylene blue and give erroneous results, but the error is not serious unless precise measurements are required.

The cation exchange capacities of some clay minerals and natural clays are shown in Table V.IV. The actual cations present are shown in some cases, but it

¹ Truog, E. and Jackson, H. L., *Proc. Soil Sci. Amer.*, 4, 136, 1939.

² Mackenzie, R. C., *J. Colloid Sci.*, 6, 219, 1951, and *Clay Min. Bull.*, 1, 203, 1952.

³ Parker, M., *Soil Sci.*, 30, 391, 1930.

⁴ Robertson, R. H. S. and Ward, R. M., *Pharmacol.*, 3, 27, 1951.

must be remembered that these apply only to the samples analysed, and may differ considerably in other specimens from the same locality. This is particularly true when comparing weathered and unweathered clays; the former are always richer in hydrogen ions although the total capacity is not usually altered substantially.

OTHER METHODS OF ANALYSIS

MANY other methods of analysis of the minerals in ceramic materials may be used, but they are not of such general application as those outlined. However, in certain specific instances, one of them may be employed with perhaps greater success than obtained by standard methods.

SPECIFIC GRAVITY OR TRUE DENSITY

THE true specific gravity of a substance is the relation between its weight and that of an equal volume of water. Its value is determined by the type of atoms or ions and the way in which they are stacked in the crystal lattice, hence the specific gravity of a pure mineral is constant for all samples and is a positive means of identification.

The specific gravity can be measured rapidly and accurately by one of the methods described in Chapter VII (p. 405) and if the material is composed of a single mineral, then it can often be readily identified. Many ceramic minerals are very similar in density, so that it is usually advisable when examining an unknown material to use specific gravity measurements in conjunction with other tests.

Different minerals of the same chemical composition can often be differentiated by measuring their specific gravity; such examples are (i) the silica minerals, quartz, cristobalite and tridymite which have values of 2.65, 2.32 and 2.28 respectively, and (ii) the aluminosilicates, kyanite, andalusite and sillimanite with the chemical composition $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ and specific gravities of 3.59, 3.18 and 3.08. The pertinent figures for many of the minerals found in ceramic bodies are given in the Appendix.

Most ceramic materials are composed of many minerals and components, so that the specific gravity is the resultant of the various ingredients. In these cases, the method is not of great value, unless the ingredients can be separated and determined singly.

HARDNESS

THE hardness of a mineral can be defined as its resistance to scratching or abrasion. It is a property which is related to the crystal structure, so, in a sense, the hardness of a mineral can be used as a means of its identification.

The hardness of a substance is a purely relative term, and it can be assessed only by comparing its abrasion resistance with that of standard minerals. Diamond, the hardest substance known, has the index 10 and others are graded down the scale to the softest, talc, with the index 1. The simplest measure of the hardness of a substance is its capacity to scratch less hard materials and, in turn, to be scratched by others less soft than itself. Other, more precise, methods are described in detail in Chapter XIV (p. 841).

In ceramic bodies composed largely or entirely of a single mineral type, the

measurement of the hardness may be a valuable guide to the composition. However, in composite bodies, as a means of mineral identification, the determination is usually of little value.

COLOUR

MANY ceramic materials are white—some like china clay, magnesia, lime, alumina, zirconia and titania are impressively so when pure. With experience it is often possible to predict the impurity content of such materials by their appearance and deviation from the pure white colour. The compounds of some elements have a characteristic colour, whereby they can be readily recognised. Iron compounds, for example, tend to impart a yellow, buff, red, brown or black coloration to bodies which contain them; cobalt and copper compounds in ceramic bodies usually give a blue and green coloration respectively. A stain or discoloration on a body may be indicative of the presence of certain undesirable minerals and should never be disregarded.

There are other properties also which can be a useful guide to the minerals in a material. These include the *odour*, the *feel* and even the *taste* of a substance which to the expert may be all-important. Properties such as the *refractoriness*, the *plasticity*, the *firing* and *drying shrinkages* may also be indicative of the content and amount of particular mineral types, but they are not usually employed for this purpose.

THE CALCULATION OF THE MINERALOGICAL ANALYSIS OF A CLAY

THERE are many methods which are of value in the detection and estimation of minerals in ceramic materials, all of which are useful in specific instances. No one method can, by itself, give a complete analysis of the minerals in any mixture, and it is only by considering the results from several that a true picture can be secured.

One difficulty which is not easy to overcome in mineralogical analyses is that naturally-occurring minerals are prone to vary in composition and properties especially if they are from different localities, and as all the methods of mineral analysis outlined are comparative, it is essential to secure a standard pure sample of each mineral to be analysed from the source being investigated. Even then, it is impossible to guarantee that each fragment of mineral will be identical, but some idea of the extent of the variation can often be obtained.

The only method which is likely to be successful in the estimation of minerals in a complex sample is to separate the individual components, to select a suitable technique from the ones outlined, which is accurate for the quantitative determination of this component and then to apply the method to the raw material.

Purely chemical methods of separation are of limited value, and satisfactory isolation of pure minerals is, in general, only achieved by physical or mechanical means, and even then treatment must not be so severe as to cause breakdown of any component.

Grimshaw and Roberts¹ have outlined a method by which the composite minerals of a natural clay may often be isolated or their nature inferred.

¹ Grimshaw, R. W. and Roberts, A. L., *Trans. Brit. Ceram. Soc.*, 51, 327, 1952.

The clay deposit should always be examined *in situ* if possible, for the type of clay, whether it be residual or sedimentary, may indicate the minerals likely to be present. The geological history and environments may be informative, for it is often possible to tell whether a clay deposit is of marine, lacustrine, fluvial or other origin. In addition, a study of the surrounding strata may indicate the nature of impurities in the clay; e.g. in sandstone areas, the clays will usually have a high free silica content, whereas clays from a predominantly limestone area will be rich in calcium carbonate.

The examination of the clay in mass sometimes reveals stratification and micaceous flakes are often observed along the bedding planes. Ironstone nodules are sometimes revealed, and occasionally large fragments of other minerals. The presence of carbonaceous material can be inferred from the colour, the remains of roots and plants, and sometimes particles of shale or coal. A hand-lens is useful in such examinations.

The next stage is to break down the clay into individual crystallites without disrupting or decomposing any mineral particles, and then to try to separate them in some way. The mildest agency is water, in which many clays break down with gentle stirring, although others may need more vigorous treatment. The addition of a dispersing agent, such as sodium carbonate or sodium hexametaphosphate, helps in the division and, occasionally, in particularly tenacious clays, the process is quickened by heating the water. Stirring must be continued until no undispersed lumps remain on decantation. At least twenty litres of water should be used for every kilogram of clay.

The resulting suspension is poured through a nest of sieves, the largest one being 60 B.S.S., the smallest 240 B.S.S. The residue on the sieves will be appreciable in many cases. The 60-mesh sieve retains a high proportion of ironstone nodules and occasionally mica flakes. The latter, however, usually predominate at lower sieve sizes along with much of the quartz and most of the heavy minerals.

The suspension which passes the sieves should be allowed to settle for 24 hours, and after decantation almost the whole of the remaining quartz and heavy minerals remain in the sediment. Washing this residue removes any retained clay or fine-particled mineral, which can be returned to the suspension.

The decanted liquid is then separated into fraction ranges by centrifugal means. Two types of centrifuge have been used. The first is a model capable of sedimenting large volumes of suspension batchwise in a large bowl. The advantage of this apparatus is that considerable quantities of liquid can be dealt with in a single operation but its range of separation is restricted as the maximum g is 490 (i.e. $490 \times$ the force of gravity).

Later stages of the fractionation are best carried out in a super-centrifuge operating under continuous feed conditions capable of producing a g of 50,000. Particles down to 0.05μ can thus be separated from suspension.

In practice it is better to split the sediment into eight or nine fraction sizes, each consisting of particles with an ever-decreasing maximum grain size. Various minerals tend to predominate in narrow particle size ranges, often with Gaussian distribution, and under controlled conditions fairly pure samples have been obtained.

By re-centrifuging, the particles can be separated into closely monodispersed fractions along the wall of the centrifuge rotor. Introducing a liner into the rotor enables the sample to be withdrawn and the grain size at any particular point calculated from nomograms as outlined by Saunders.¹

In this way the various minerals in clays can be separated into grain size zones, which by suitable treatment can be further purified.

Although sedimentation and centrifuging methods have gone a long way towards completely separating the minerals in a clay, it is frequently impossible to isolate pure specimens by these means alone. This is particularly the case in the fractions of larger grain-size where three or four minerals sometimes predominate over a specific particle size range. Other separation methods must therefore be employed.

(i) **Selective Chemical Action.** This can be used where one component of a mixture of minerals is unattacked by a certain chemical reagent which effectively removes the rest. The chemical method for estimating quartz is such an example.

Other methods employ the reverse principle of dissolving one component preferentially to others, as, for example, dilute acid solution of carbonates, and the Hallimond method of estimating chlorites.²

(ii) **Heavy Liquid Separation.** The use of organic liquids to separate minerals of different densities is well known. In general only comparatively large-sized particles are efficiently isolated by density difference methods. Smaller sizes tend to flocculate in organic liquids and so restrict free sedimentation.

(iii) **Froth Flotation.** By the use of a suitable frothing agent some separation of minerals can be obtained. The most suitable are amino-acids of high molecular weight, and with these mica and quartz can be separated. A full account of froth-flotation methods is given by Perry.³

(iv) **Electrostatic Separation.** The principles of electrostatic separation have been illustrated by A. L. Johnson.⁴

Briefly, many minerals if allowed to fall freely between two oppositely charged plates, will move towards one or the other. Muscovite mica, for example, can be deflected appreciably by comparatively low applied voltages (about 3,000 V.) and the electrostatic separation of feldspar from quartz is carried out commercially in the United States.

Unfortunately many of the minerals commonly associated with clays behave similarly in an electric field and a very high voltage is required to achieve satisfactory separation.

(v) **Magnetic Separation.** This is useful in a limited field. Should there be any large-sized particles of haematite or similar magnetic mineral, easy separation is secured.

(vi) **Elutriation.** Elutriation has proved effective for separating fine-grained fractions from the centrifuge into very closely monodispersed ranges, with subsequent purification of mineral species.

¹ Saunders, E., *Ind. Eng. Chem. (Anal.)*, 20, 379, 1948.

² Loc. cit., p. 215.

³ Perry, J. H., *Chemical Engineer's Handbook* (McGraw-Hill, N.Y., 1952).

⁴ Johnson, A. L., *Amer. Inst. Min. Met. Tech. Paper*, 677, 1938.

A stream of water or air is passed upwards through a bed of dispersed particles and, if the flow is carefully regulated, particles within a narrow size range can be extracted. The separation of large particles is not very effective because the liquid flow rate has to be high; consequently turbulence influences the separation and the volume of liquid is excessive. This method will be described in more detail in a later chapter.

Although a sample of the pure minerals can be obtained with the methods outlined, it is usually impossible to effect quantitative separation of all fragments of that mineral. Therefore a test must be selected which is suitable for the estimation of each mineral present in the presence of the impurities. The isolated pure sample is used for standardisation purposes.

In many cases, all the principal and some of the accessory minerals in a clay can be estimated in this way. Another important conclusion which can be derived is the grain-size range of any mineral in the raw material.

A mineral balance sheet should be drawn up to compare with the full chemical analysis which is an essential. If the two do not agree then some important mineral constituent has not been detected or has been assessed incorrectly. Frequently some mineral defies estimation, in which case it can be established only by difference.

The above basis for the separation of components in a clay has proved excellent in assessing the mineralogical composition and the grain-size distribution of different species. Certain minor modifications have been necessary in some cases, but the same general methods have been of value for clays of many types.

CHAPTER VI

THE CHEMICAL AND MINERALOGICAL COMPOSITION OF CERAMIC RAW MATERIALS¹

CERAMIC materials can seldom be termed pure. Although, in some, one mineral type may predominate, the 'impurities' present may be all-important in determining its properties. Clays, in particular, contain many mineral types and are extremely variable in composition. So complex is their study and so great are the difficulties involved, that, although clays are the most extensively used of all ceramic materials, very few have been scientifically examined and the complete details of their mineralogical and chemical composition derived.

For many centuries it has been possible to manufacture beautiful pottery and many useful articles such as bricks, tiles, crucibles, stoneware vessels and furnace linings without it being necessary to have any formal knowledge of their constitution. This is still true of many clays used for making common bricks, tiles, terra-cotta, coarse earthenware and some of the simpler forms of pottery (e.g. peasant ware).

Present day manufacture, with its precision methods and bulk production techniques, necessitates a complete understanding of all the factors involved in the processing of ceramic ware of most types. Not least of these requirements is a knowledge of the raw materials themselves, the mineral types that are present and how their physical state and chemical nature can influence the properties during manufacture and in use.

In the refractories industry, increasing demands are being made by the user in the metallurgical, carbonising and other industries for materials capable of withstanding more severe conditions. To meet this need, great attention must be paid to the raw material and rigid control is essential. Tremendous improvements in the quality of silica bricks have been made over the last few years, simply by appreciating the role of the various components present in the raw material on the properties of the fired product. The elimination or reduction in amount of deleterious impurities has done much to improve the quality.

The scientific approach to clay problems has not, as yet, been quite as fruitful as it has in other ceramic fields, principally because of the greater complexity encountered. Because clays consist essentially of many different mineral types, most of which are in the form of minute particles, their examination is difficult even when using modern experimental methods. A further cause of difficulty is the influence of the particle size distribution of the various minerals on the properties of the clay. This is often as important as the type and amount of the minerals themselves.

¹ For convenience some materials which are not strictly 'raw' (e.g. bodies, engobes glazes) but are compounded from several ingredients, are included in this chapter.

THE COMPOSITION OF CLAYS

IN their natural state, clays consist of:

(i) Minerals of primary origin, i.e. those present in igneous rocks and which have undergone no significant alteration in composition. These may be described as *primary minerals* (see p. 285).

(ii) Minerals of secondary origin produced by the action of chemical and physical agents on primary minerals resulting in their breakdown and conversion to *secondary minerals*.

Both primary and secondary minerals occur in clay deposits in many different proportions. The *residual clays*, which have undergone little or no transportation, usually contain a much larger proportion of primary minerals, whilst the *sedimentary clays*, which have been transported and deposited perhaps many times, contain few, if any (except quartz), of the minerals associated with igneous rocks.

In composition, clays consist of *clay minerals* (described in Chapter III), together with varying proportions of other substances commonly known as *impurities*—a term which is not always appropriate because the presence of some so-called impurities is of great technical importance in the use of certain clays. For instance, the pleasing red colour of some *terra-cotta*, the imperviousness of *stoneware* and its resistance to corrosion, the delicate translucency of *chinaware* and *porcelain*, the enormous resistance to crushing of some *engineering bricks*, and the extraordinary resistance of *electric insulators* are all due to the presence of a suitable proportion of certain 'impurities' which impart to these materials their valuable characteristics.

A pure clay mineral may be highly refractory, but it may be very weak when burned, owing to the absence of suitable 'impurities' which would, if present, form a vitrifiable bond to unite the clay particles into a mass of great strength.

The proportion of impurities allowable in a clay depends on the purpose for which it is to be used. Thus for the manufacture of *whiteware*, the clay must not contain a harmful proportion of colouring impurities, such as iron oxides; similarly, where a clay is to be used as a refractory material it must be as free as possible from fluxes (p. 345), as these would reduce its resistance to heat.

As a chemical analysis does not reveal the state in which the various substances are combined, it is very important when considering the results of analyses of clays, silica rocks and other materials containing aluminosilicates, to remember that the proportion of fluxes shown by such analyses does not represent the total amount of impurity present; the silica and alumina with which the fluxes are combined (or with which they will combine when the material is heated) will be included in the total amounts of silica and alumina, so that the presence of 1.6 per cent of potash may represent 10.0 per cent of impurity in the form of feldspar, the 1.8 per cent of alumina and the 6.6 per cent of silica being included in the total silica and alumina present. Hence, a clay which contains a very small percentage of lime, magnesia, potash, and soda may actually contain a large proportion of minerals other than clay. For this reason, it is often more important to know the mineralogical composition of a clay or other ceramic material than its composition as shown by chemical analysis.

The effects of impurities in a clay depend upon:

- (a) Their nature and behaviour when the clay is used.
- (b) The proportions in which they occur.
- (c) The size and shape of the grains of clay and of the impurities.
- (d) The conditions under which interaction takes place, including (i) the temperature reached, (ii) the duration of the heating, (iii) the atmosphere of the furnace or kiln, and (iv) the effect of any other substances which may be present.

The principal components in clays may be classed as follows: (a) silica; (b) alumina; (c) alkali-bearing minerals; (d) iron compounds; (e) calcium compounds; (f) barium compounds; (g) magnesium compounds; (h) titanium compounds; (i) manganese and other compounds which occur in small proportions in some clays; (j) complex alumino-silicates often containing other elements; (k) carbonaceous matter; (l) moisture and colloidal water (i.e. water of constitution and of crystallisation); (m) exchangeable bases.

Various other impurities which occur in some clays are usually of minor importance.

Silica occurs in clays and allied minerals (a) in the *free* state, as quartz or other form of crystalline silica and as amorphous, hydrated, or colloidal silica, and (b) *in combination* (i) with alumina in the form of clay and other clay minerals, (ii) with fluxes and alumina in the form of feldspar, mica, or other aluminosilicates, or (iii) with various bases forming simple silicates, such as wollastonite (CaOSiO_2), etc.

The effects of free silica in clay are as follows:

1. It reduces the plasticity.
2. It lessens the shrinkage on drying and firing.
3. It reduces the tensile and crushing strengths, unless it is of small particle size.
4. It reduces the refractoriness in many cases, though not in all.

The size of the grains of silica is also important, as very small particles will often react and act as a flux under conditions where larger particles of silica increase the refractoriness of the mass. In some cases, silica will increase the refractoriness of a clay, quite apart from the size of the particles, especially if the 'clay' is very impure; any improvement which may be effected in this manner by the addition of silica is of very limited extent. Seger found that, with pure clay and pure silica, the melting-point is lowered with an increase in the proportions of silica until a molecular ratio corresponding to $\text{Al}_2\text{O}_3:17\text{SiO}_2$ is reached, after which further additions of silica raise the melting-point; this closely corresponds to the values predicted from the equilibrium diagram of alumina and silica.

Free silica occurs in clays of most types. In residual clays, it is present mainly as crystalline *quartz*, for this is a common constituent of igneous rocks and is unaltered by normal weathering processes.

Sedimentary clays also often contain appreciable amounts of quartz which has been transported and deposited along with the clay minerals. In them, the content of free silica is very rarely entirely quartz, because during transportation the original crystalline material may have been subjected to mechanical breakdown which not only reduced the grains in size, but may have converted the quartz into distorted, crypto-crystalline or amorphous varieties. Furthermore, some finely-divided silica

may have been dissolved and later precipitated again under more favourable conditions. Such processes are common, for *flint*, *agate*, '*drusy*' *quartz* and pockets of well-developed quartz crystals are formed in this way. When reprecipitation is rapid, the silica formed will be amorphous or crypto-crystalline, and although it may be compacted and metamorphosed at a later stage in its geological history, it may never develop the crystallinity or lattice configuration of quartz. Material of this type is of common occurrence, *chalcedony*, *flint*, *opaline silica* are but a few examples, of what may be present as 'free silica' in clays. These minerals do not give the same X-ray or thermal pattern as quartz crystal, and it is always unwise to accept the quartz content, determined by these methods, as the total amount of free silica.

Silica which is not in the form of quartz is much more reactive than is crystalline quartz; it also converts more readily to cristobalite and tridymite, and will combine with fluxing agents at appreciably lower temperatures.

Alumina. Alumina occurs in clays in the form of clay minerals, feldspars, mica, hornblende, tourmaline, and other similar aluminosilicates, all of which are moderately fusible; free alumina is also found in some clays, derived from bauxites and laterites. Halloysite clays frequently contain associated free alumina in the form of *gibbsite* ($\text{Al}(\text{OH})_3$). Such clays are highly valued for refractory purposes, especially if the total alumina content is high.

Other clays may contain free alumina either as *gibbsite*, *diaspore* ($\text{AlO} \cdot \text{OH}$) or as a *colloidal* variety. Some fireclays, particularly of Scottish origin, often have a higher alumina content than would be indicated from the rational analysis.

Aluminous compounds, other than clay minerals, have the following **effects on clays** in which they occur:

1. They reduce the plasticity of the clay, as they are non-plastic.
2. They increase the refractoriness of a clay, provided that the total proportion of alumina is greater than 5 per cent. The refractoriness of a silica brick is drastically reduced by alumina. For each 0.1 per cent of alumina which is present in silica, the maximum operating temperature of the refractory is reduced by about 10°C .

L. Bertrand¹ found that raw clays containing more than 29 per cent of alumina, or fired clays containing more than 32 per cent, had softening points over 1650°C . Those containing 20–29 per cent of alumina in the raw clay, or 21–32 per cent in the fired material, had softening points often above and sometimes lower than 1650°C . Clays with less than 20 per cent of alumina (or 21.5 per cent in the fired material) generally soften at temperatures below 1650°C ., though occasionally such clays are found which soften above this temperature.

Alkalies and other fluxes are usually associated with alumina compounds and these usually have a serious influence on the refractory properties.

Alkali Compounds. The chief alkalies in clays occur as:

1. Silicates or aluminosilicates of which *feldspars*, *micas* or *hydrous micas* are the chief examples. The last-mentioned minerals which are the principal alkali-bearing constituents in many fireclays are classified as a clay mineral, but, unlike those of the

¹ Bertrand, L., *La Céramique*, 25, 153, 1922.

kaolin and montmorillonite group they contain alkali as an integral part of their structure. The influence of such minerals on the properties of clays is discussed in Chapter VIII, but the presence of an alkali-bearing mineral always reduces the vitrification temperature and the refractoriness.

2. Adsorbed cations on the surface of clay mineral crystals. The degree of adsorption depends on the available surface area and on the nature of the clay minerals. Montmorillonites may have up to 3 per cent of alkalis from this source, but kaolin clays rarely have more than 0.3 per cent (see also p. 291).

3. Soluble salts, such as *potassium sulphate*, *sodium sulphate* and *sodium chloride*. These salts also reduce the refractoriness of the material; they may also, if present in sufficiently large proportions, form a white scum on the surface of the articles either before or after firing. Soluble salts also affect the plasticity of clay, some tending to increase it, though most of them reduce it.

In stoneware, porcelain, and other vitrified ware, the higher the molecular proportion of potash or soda, the more fusible is the mass. In incompletely sintered ware, such as faience and earthenware, the larger the proportion of potash or soda the more solid will be the body after firing at a certain (finishing) temperature. **The chief effect of alkalis** in clays is to reduce the refractoriness or vitrification temperature. They combine with alumina and silica to form liquids at low temperatures (c. 700° C.) and consequently are termed *fluxes*. The liquid which forms on firing in clays containing alkalis does not crystallise readily on cooling but forms a glass, which behaves as though it were a super-cooled liquid.

Because of the readiness of liquid formation, alkalis impart imperviousness and strength to fired clay bodies and are a major constituent of earthenware, stoneware and porcelains.

Soluble alkali salts may have an important influence on the colloidal and plastic properties of clays (see Chapter VIII).

Most alkali-bearing minerals are non-plastic and, for this reason, they reduce the green and dry strengths of bodies which contain them. They reduce the drying shrinkage of clays and, in general, facilitate the drying process by preserving an open texture.

Alkali minerals in clays can usually be identified by either microscopic or X-ray methods.

Iron Compounds. The various iron compounds which may occur in clays may be classed as (a) ferric oxide (Fe_2O_3); (b) ferrous oxide (FeO); (c) magnetic iron oxide (Fe_3O_4); (d) iron sulphides (FeS and FeS_2); (e) iron carbonates (FeCO_3); (f) ferrous and ferric hydroxides, which behave like the respective oxides; (g) ferro-silicates and ferro-alumino-silicates; (h) ferrous aluminate (*hercynite*); and (i) soluble iron salts (chiefly ferrous sulphate).

The principal iron-bearing minerals in clays are:

Magnetite, Fe_3O_4 , which occurs as black cubic crystals, with a hardness of 5.5–6.5 and a specific gravity of 4.9–5.2. Magnetite is seldom present in raw clays, but is produced by the partial reduction of ferric oxide during the burning of some clay wares. It is common in some bricks and is readily detected in the ground material by its magnetic properties.

Haematite, Fe_2O_3 , occurs as steel-grey, iron-black or reddish hexagonal crystals, or as red amorphous particles, with a hardness of 5.5–6.5 and a specific gravity of 4.5–5.3. It is not often present in clays which have been much exposed to the weather, as it is readily converted into the hydrated form—*limonite*. In burned clays it is one of the most important colouring agents, especially in red bricks, terra-cotta, etc. Haematite is a constituent of some clays, however, and colours them characteristically red or salmon-pink.

Limonite, $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, is a hydrous iron oxide occurring as yellow or brownish amorphous particles, with a hardness of 5–5.5 and a specific gravity of 3.6–4.0. The term limonite is not confined to a single, definite, chemical compound, but includes an apparently large number of compounds of variable composition, which are probably colloidal in nature and contain varying proportions of water. The formula by which limonite is usually expressed is $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, but the term is applied to almost any hydrous iron oxide. It is very common in clays and forms one of the principal yellow or buff colouring agents in the raw material. Limonite occurs frequently in clays which have been weathered, and many surface clays and weathered outcrops owe their colour to it. It may be present as (a) a film over the grains of clay or sand, or (b) as irregular nodules scattered through the mass.

On heating, limonite evolves water and forms red ferric oxide. Hence, like the latter, it is a very important source of the red colour to which many clay products owe their characteristic appearance.

Goethite, $\text{FeO}(\text{OH})$ or $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, is a hydrous iron oxide which forms brownish-black, yellowish or reddish orthorhombic crystals, or occurs in the massive or fibrous state with a hardness of 5–5.5 and a specific gravity of 4.4–4. It is of common occurrence in many clays, where it is often distributed in a colloidal form round particles of other minerals. Much of the so-called limonite in clays is finely-divided goethite.

Lepidocrocite, or $\gamma\text{-FeO} \cdot \text{OH}$, is not thought to be of common occurrence in clays, but it may be a minor constituent in some fireclays.

Turgite, $2\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, is a similar hydrous iron oxide, which produces a red streak as distinct from the brownish or yellowish streak of goethite. It also contains less water.

Ferrous oxide, FeO , does not occur in raw clays, but it may be produced during the burning of the clay in a reducing atmosphere.

Pyrites—a general term for all iron sulphides—includes three important minerals, *pyrite*, *marcasite* and *pyrrhotite*.

Pyrite, FeS_2 , is a sulphide of iron occurring as yellowish cubic crystals, having a hardness of 6–6.5 and a specific gravity of 4.8–5.1. It is sometimes disseminated in minute grains through the raw clay, or it may form large nodular or fibrous masses, or it may occur in masses resembling small petrified roots; the last-named are sometimes known as *race*. When heated to redness, pyrite evolves half its sulphur and later combines with part of the silica in the clay, forming a silicate (*fayalite*, see p. 108), which readily melts to a dark fluid slag. This slag, even when finely ground, forms unsightly blotches, the size of which depends on the size and proportion of the grains of pyrite.

Marcasite, FeS_2 , is similar in composition to pyrite, but forms radiating needles

of orthorhombic crystals. It occurs chiefly in the form of fibrous masses or nodules in the same manner as pyrite. Marcasite is readily oxidised to ferrous sulphate on weathering, and later forms a whitish scum on the dried clay. Pyrite, on the contrary, is not so easily weathered and oxidised.

Pyrrhotite, $\text{Fe}_n\text{S}_{n-1}$, is a sulphide of iron forming red, brown, bronze or copper-coloured hexagonal crystals or occurring in the massive state, with a hardness of 3.4-4.5 and a specific gravity of 4.4-4.65. It is not of frequent occurrence in clays.

Iron sulphides are most common in the Coal Measure fireclays and in ball clays, though they also occur to a variable extent in other clays. Unlike iron oxides, carbonates, and sulphates, they do not form a pleasant red colour on the ware in the kilns, but produce small black spots if the grinding has been sufficiently fine; otherwise, they form relatively large masses of fused slag.

Copper-iron sulphides, chiefly in the form of *chalcopyrite*, CuFeS_2 , *bornite* and *erubescite*, occur in some fireclays, the principal occurrences in this country being in Northumberland, Durham, South Scotland, North Staffordshire and Shropshire. These copper compounds act in a similar manner to iron pyrite, except that they produce greenish-black slag patches instead of black ones.

Ferrous sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (*copperas*), occurs in some clays as a soluble salt. It is often produced by the weathering of sulphides of iron and it has the same general properties as ferrous carbonate but is more soluble and can cause *scum* or *efflorescence* (see p. 831).

Chalybite or *siderite*, FeCO_3 , is an iron carbonate occurring as yellow, brown, or red hexagonal crystals, with a hardness of 3.5-4.5 and a specific gravity of 3.7-3.9. It is present in large proportions in the Clay Ironstone of British coalfields, in the Staffordshire marls and in the Coal Measure fireclays. Chalybite is found in three forms in clays: (a) as a film coating the other mineral grains; (b) as minute crystals; and (c) as concretionary masses, sometimes of large dimensions consisting of chalybite or clay iron-stone. Nodular fragments of siderite and of pyrites are the principal source of 'iron-spotting' in fireclay bricks and in other ceramic ware made from these types of clay.

Vivianite, $\text{Fe}_3\text{P}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$, is a hydrous phosphate of iron in the form of blue, white or green monoclinic crystals, with a hardness of 1.5-2 and a specific gravity of 2.66. Vivianite occurs to a very small extent in boulder clays as minute blue crystals, but the proportion is usually negligible.

Many other minerals, including silicates and aluminosilicates, such as hornblende, hypersthene, augite, olivine, fayalite, glaucophane, glauconite, etc., which occur in clays also contain a variable proportion of iron compounds.

The ferruginous minerals in clays occur as (a) large masses scattered irregularly through the mass; (b) minute grains uniformly distributed; and (c) stains on the surface of the grains. Those in group (a) may be removed fairly readily by hand-picking, but the other two forms are almost impossible to remove.

In thin sections of articles made of burned clay, the decomposition products of limonite, haematite, and many other iron compounds may be recognised under a microscope (the section being illuminated by reflected light) as brown or reddish-brown specks where the material has been fired in an oxidising atmosphere, and as

bluish-black films where a reducing action has occurred. The other minerals present are frequently enveloped by a film of iron oxide.

Pyrite is never seen in microsections of properly burned clayware, as it is decomposed at a comparatively low temperature, forming the vitrified, slag-like material (fayalite).

The identification of iron compounds in clays is not always easy, especially in those cases where they are present as a colloidal film. Hydrated varieties give a characteristic peak in differential thermal analysis and goethite is readily identified and estimated by this means. Large particles of iron-bearing minerals can often be identified under the microscope. The total amount of iron in a clay is readily determined by chemical methods; occasionally, iron can be quantitatively extracted by treatment with dilute hydrochloric acid. Chemical analysis does not reveal the identity of the iron-bearing compounds nor differentiate between colloidal and large-particled material.

The **principal effects of iron compounds** in clays are:

- (i) They effect an alteration in the colour.
- (ii) They may reduce the refractoriness of the clay.
- (iii) Soluble iron compounds may form a scum on the ware.
- (iv) They may form iron spots which are clearly visible in the burned clay.

Such localised concentrations of iron are usually the result of nodular fragments of ironstone. They seriously influence the behaviour of the ware in an atmosphere of carbon monoxide at certain temperatures, for they catalyse the precipitation of carbon which may disrupt the brick. This is thought to be the cause of *scurfing* in alumino-silicate refractories used in gas retorts; it is only noticeable when the iron is present in localised centres of high concentration.

Even very small quantities of iron oxide are undesirable where white ware is required, unless there is a comparatively large proportion of calcium carbonate in the clay. The colour normally produced by the iron compound will then be neutralised on heating, and a cream product formed instead of the usual red colour due to ferric oxide.

Ferric oxide does not greatly reduce the refractoriness of a burned clay, provided it is always maintained in an oxidising atmosphere, for it is highly refractory. In a reducing atmosphere, on the contrary, it acts as a powerful flux.

Magnetic and ferrous oxides are very undesirable, as they are powerful fluxes, and combine with clay to form viscous, fusible silicates, ferro-silicates, and alumino-silicates, the most fusible silicate being *fayalite* (melting-point, 1150–1210°C.) and the most fusible alumino-silicate, corresponding to the formula $5\text{FeOAl}_2\text{O}_3\cdot 5\text{SiO}_2$, which melts at 1073°C.

Ferrous carbonate, when present in a clay, may either be reduced in the burning process to ferrous oxide with the evolution of carbon dioxide (the oxide then acts as a flux, combines with the silica in the clay and produces black, slaggy masses of fusible silicates which are very undesirable), or it may be oxidised to ferric oxide, and be comparatively harmless unless white ware is required.

Ferric sulphide (pyrite), when heated, loses half its sulphur at 400–600° C. and the rest at a higher temperature. In a reducing atmosphere it produces ferrous

oxide which acts as a powerful flux, but if the burning is carried out entirely in an oxidising atmosphere, the iron may be completely oxidised to form ferric oxide, which does not greatly affect the refractoriness of the clay.

Ferro-silicates and ferro-alumino-silicates behave in a manner similar to feldspar, i.e. they are moderately fusible and increase the amount of vitrified matter or 'bond' in the fired ware and so slightly increase the strength of the ware. According to their colour they may improve or spoil the appearance of the ware. Some ferro-silicates, such as *nontronite*, are decomposed into their constituent oxides when heated.

Soluble iron compounds often produce a light-coloured *scum* on the surface of the dried ware. On burning, this is usually converted into unpleasant brown or black patches.

If small amounts of iron compounds are uniformly distributed throughout a clay they have little influence on the refractoriness and are deleterious only in so far as they affect the colour. They react with the clay to form silicates or alumino-silicates on prolonged firing.

Calcium Minerals. The *chief* calcium compounds in clays are (a) *calcite* (CaCO_3), which occurs as white or grey hexagonal crystals, with a hardness of 3 and a specific gravity of 2.71, or as amorphous grains; (b) *aragonite* (CaCO_3), which occurs as white, grey or greenish orthorhombic crystals, with a hardness of 3.5–4 and a specific gravity of 2.94, or as amorphous grains; calcium carbonate may be present in the form of chalk or other form of limestone and occasionally fragments of shells may be observed, and (c) various *calcium silicates* and *alumino-silicates* which include some feldspars, micas and other primary minerals or their alteration products. Residual clays derived from an igneous rock are more likely to contain such mineral impurities, for most of them are readily decomposed by weathering and water transportation.

Calcium compounds also occur in much smaller proportions in clays in other forms, including:

Gypsum (*calcium sulphate*, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) occurs in some clays and shales in the form of colourless, white, grey, yellow or reddish monoclinic crystals, with a hardness of 1.5–2 and a specific gravity of 2.3. *Selenite*—another variety of gypsum—is more common in clays, especially in the London and Oxford clays, and in some shales.

Anhydrite (CaSO_4), is often regarded as a variety of gypsum. It rarely occurs in clays, but is sometimes found in those of the Lias formation.

Apatite, a crystalline *calcium phosphate*, occasionally occurs in clay, as also may coprolites and other calcium phosphates of organic origin. In burned clays various other complex calcium compounds may occur, such as calcium ortho- and meta-ferrates.

The **chief effects of calcium compounds** in clays are:

(i) They act as fluxes, i.e. they combine with alumina and silica to form low melting-point liquids, and so they reduce the vitrification temperature and refractoriness of the clay.

(ii) They produce a mobile, fluid liquid of great corrosive power. When cooled, the liquid readily forms a glass which acts as a strong bond and also

produces impermeability and resistance to acids and other chemicals. The glass softens at a comparatively low temperature and may cause serious distortion of the body.

(iii) At temperatures below that at which they react, calcium compounds may reduce the shrinkage of a clay and facilitate its drying.

(iv) At a dull red heat, calcium compounds may combine with iron minerals and 'bleach' the red colour which they normally produce on firing to a white cream, or buff. To be most effective, the calcium minerals must be finely divided and disseminated throughout the clay.

(v) Calcium carbonate, when heated to about 900°C . is converted into lime, which, if it remains uncombined on cooling, may absorb moisture from the air and swell so much as to crack or burst the body. This is a serious defect in some clays used for brick-making.

(vi) Calcium sulphate is stable on firing and may remain as such in low-fired bricks. It is one of the most frequent causes of scum and efflorescence in common and facing bricks. Although not of common occurrence in natural clays, calcium sulphate is often formed on firing in clays containing calcium carbonate and pyrites.

(vii) In some brick-making clays, calcium compounds, in small amounts, increase the vitrification range.

(viii) As a fluxing agent in bodies and glazes, calcium compounds reduce the expansion but raise the maturing temperature, when they replace alkalies.

(ix) Calcium phosphate, when mixed with silica and heated to redness, exchanges phosphorus pentoxide for silica, and forms a calcium silicate having the same properties as that produced by the action of lime on silica.

(x) Calcium silicates and some other stable calcium compounds melt at a comparatively low temperature, and then act as fluxes in a manner similar to lime, but much more slowly. The calcium aluminosilicates produce a tougher and more viscous bond than the simple silicates, and are, therefore, preferable in some types of bonding.

(xi) Calcium aluminates are not abundant in clays, but may be formed when a mixture of clay and a lime compound is heated. They act as mild fluxes.

According to Pukall, a high proportion of lime in a clay causes fritting and fusion rather more slowly than an equally high proportion of potash. Thus, with the same total molecular ratio of bases ($\text{RO} + \text{R}_2\text{O}$) to alumina and silica, a high molecular proportion of potash will form a stoneware at about 1230°C ., whilst a high molecular proportion of lime will produce a good earthenware. At very high temperatures, both these mixtures will produce porcelains, unless the alumina or silica is excessively high.

According to Dorfner, the higher the molecular proportion of lime in the bases, the total RO being constant, the less fusible is the product if a porcelain, stoneware, or other vitrified ware is being produced; but in a porous ware, the higher the molecular proportion of lime in relation to the total bases (RO), the more friable will be the ware and the less the liability of the glaze to craze.

Acid soluble calcium salts, e.g. carbonates are readily detected and sometimes estimated by selective chemical analysis. Carbonates and sulphates of calcium may

be identified by differential thermal analysis, but complex aluminosilicates, e.g. feldspars, micas, can be detected only by microscopic or X-ray techniques. The total calcium content of a material can be rapidly assessed by spectrographic analysis.

Barium Compounds are not of frequent occurrence in clays, the only one of any importance being *barytes* (*barium sulphate*, BaSO_4), which may be present as colourless, white, yellow, red, brown or blue orthorhombic crystals with a hardness of 2.5–3.5 and a specific gravity of 4.5. Barytes sometimes occur as the cementing medium in clays and shales, as at Seaton and other districts in Northumberland.

Barium silicates and aluminosilicates are of rare occurrence in clays but barium is revealed as a trace element in clays from many localities by spectrographic methods.

Barium compounds in clay behave similarly to those of calcium on firing.

Strontium minerals seldom occur in appreciable quantities in clay, the only one likely to be recognised being *celestine* (strontium sulphate, SrSO_4), which exists as white orthorhombic crystals, with a hardness of 3–3.5 and a specific gravity of 3.96.

Magnesium minerals occur to a small extent in most clays, chiefly as *magnesite*, MgCO_3 , *dolomite*, $\text{MgCa}(\text{CO}_3)_2$, *spinel*, *cordierite* and as various magnesium silicates and aluminosilicates. *Magnesite* is sometimes found in clays as fibrous crystals, but generally the grains of magnesium compounds are too small to be recognisable as they are difficult to separate mechanically and the proportion is almost invariably less than corresponds to 3 per cent of magnesia.

Magnesium sulphate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (Epsom salts), is present in small amounts in some clays for brickmaking, but even 0.05 per cent can spoil ware, because it produces a white efflorescence, which in time disrupts the body. It can be rendered harmless by adding finely-divided precipitated barium carbonate to the clay before moulding. Magnesium sulphate is sometimes formed during firing by the combination of other magnesium salts with sulphurous fumes. In this case, barium compounds are ineffective in eliminating efflorescence.

Because they are usually of fine particle size and present in small amounts, magnesium compounds in clays are difficult to identify. The carbonates and sulphates can be detected by selective chemical methods or by differential thermal analysis; other forms can occasionally be identified by optical or microscopic methods.

Magnesium compounds act as fluxes and reduce the refractoriness of clays in which they occur, though they are less powerful than the corresponding lime compounds and act more slowly. As a consequence, they are usually less harmful and less likely to cause loss of shape when heated. The slag produced by the action of magnesium compounds on clay is also more viscous than that produced by calcium compounds and this further restricts the occurrence of a rapid loss of shape.

Zinc compounds do not occur in significant proportions in clays. Their action on clays (e.g. in the distillation of zinc in fireclay retorts) can be serious (see Chapter XIV). **Titanium minerals** being very resistant to the action of the weather, are fairly common in most clays, the chief ones being *rutile*, *anatase*, and *brookite*, all of which have the formula TiO_2 . Occasionally *sphene* (*calcium titanite*) crystals, CaTiSiO_5 , and sometimes *ilmenite*, FeTiO_3 , are present. The total content seldom exceeds the

equivalent of 3 per cent of titanium oxide, and in many highly plastic clays less than 1 per cent of titanium oxide is present. A few 'bastard' fireclays contain as much as 10 per cent of titanium oxide.

The oxides of titanium are the usual form of mineral. Brindley¹ has reported that *anatase* is the common form in some sedimentary clays, but *rutile* predominates in many residual clay samples.

Titanium compounds are very persistent and often remain quite unaltered in clays and other materials which have been fired at 1300° C.; they act as feeble fluxes, although they are not active below 1500°. In glasses and glazes they are powerful opacifiers.

Chromium minerals sometimes occur to a very small extent in clay, usually in the form of *chromite*.

Tin-bearing minerals are seldom present in clays, though occasionally *cassiterite* (SnO_2) is found as black or brown tetragonal crystals, with a hardness of 6-7 and a specific gravity of 6.4-7.1.

Manganese minerals occasionally occur in clays, chiefly as a thin film of oxide on the other mineral grains.

They act as fluxes and in many respects resemble ferrous compounds but their amount is usually too small to be serious. The chief effect of manganese is in staining articles made from clays which contain them, the colours of the stains ranging from a medium brown to dark brown or black. Sometimes manganese dioxide is added to clays used for making facing or blue engineering bricks to produce dark colours, low porosity and an increase in crushing strength. They are often added to sand for facings and to veneer compositions.

Vanadium compounds in clays are rare, but, as they sometimes cause a green discoloration in buff-burning clays and pipe clays and occasionally give rise to a green efflorescence in bricks, their presence must not be overlooked.

The minerals of titanium, chromium, tin, manganese and vanadium are usually of high density and they can often be isolated by heavy liquid separation and then identified.

Sulphur compounds in clays are chiefly *pyrites*, and various sulphates, particularly of calcium, magnesium and sodium. In many instances, the precise form of the sulphur compounds in a clay may be of little importance but the total percentage (found by chemical analysis) may be very useful in indicating the source of discoloration, scum or efflorescence.

Small amounts of sulphur compounds may be a major factor in the bloating of low-grade fireclays and other clays at temperatures about 1150° C. In clays rich in iron, sulphur compounds are often responsible for producing 'black-hearts' by maintaining the iron in a reduced state. This is often confused with the residue from undecomposed carbonaceous matter (see p. 291), but it can be distinguished by its steely appearance and the sharp line of demarcation between the black zone and the surrounding red colour of the fired clay.

Phosphate minerals are found in some clays, the most important is *apatite*, a complex calcium phosphate containing proportions of chlorine and fluorine. The formula is usually expressed as $\text{Ca}_5(\text{F}, \text{Cl})\text{P}_3\text{O}_{12}$ and it occurs as blue, grey, red,

¹ Brindley, G. W. and Robinson, K., *Min. Mag.*, 28, 244, 1947.

brown, green or yellowish hexagonal crystals, with a hardness of 5 and a specific gravity of 3.17–3.23.

Coprolites and *phosphorite* are natural phosphates produced by the accumulation of organic remains or fossilised animal excreta. Phosphatic *nodules* of this nature are common in the Greensand beds, and true coprolites are found in the Oxford clay and Gault formations.

Complex Alumino-silicates. The principal impurities in clays are complex silicates or alumino-silicates usually containing other elements as principal ingredients. Clays are secondary products which have resulted from the breakdown of igneous rocks. Many primary minerals in these rocks are relatively easily attacked by epi- or hypo-genic agents and converted into some other form. Clays will, therefore, contain minerals of many types, some of which will be unaltered *primary* forms, whilst others will be the *secondary* breakdown products of such minerals. The so-called *residual* clays are more liable to be contaminated with true primary minerals than those of *sedimentary* character where successive transportations and depositions have increased the possibilities of breakdown.

PRIMARY MINERALS IN CLAYS

The **three most important primary minerals** in clays derived from igneous rocks are quartz, feldspars and micas, but olivines, pyroxenes and other complex minerals may also be present.

Quartz is a common mineral in clays and for a full description see p. 315.

Feldspar is the name given to a group of alumino-silicates containing one or more of the following metals as bases: potassium, sodium, calcium and barium. The feldspars (p. 167) form isomorphous mixtures and, consequently, may vary greatly in composition, especially as regards the metals present. They are common in residual but seldom in secondary clays for they break down very easily under normal weathering conditions. The principal types have been outlined in Chapter III (Table, III–XIII).

When pure, the feldspars are colourless or white, but most specimens are tinged reddish-grey, green or blue because of occluded or dissolved impurities. They have a hardness of about 6 and a specific gravity of 2.5–3, and may usually be recognised by their characteristic cleavage or twinning.

Feldspars are frequently found in foreign kaolins and, as china stone (p. 322) is fairly rich in unchanged mineral they are present in small amounts in crude English china clays. It is most unusual to find them in sedimentary clays for they are readily changed to other minerals as described on p. 292.

Feldspars contain large proportions of alkali or alkaline earth elements; consequently they melt at comparatively low temperatures (between 1200° and 1250° C.) and act as powerful fluxes in ceramic bodies. It is not uncommon to find well-developed feldspar crystals in fired ceramic bodies which are rich in calcium or alkalies, for they are a common product of the crystallisation of molten alumino-silicates.

Mica is a term used to designate a group of minerals crystallising in the monoclinic system in characteristic plate-like masses or particles, and consisting of alumino-silicates of potassium, sodium, lithium, iron and magnesium.

The principal micas have been outlined on p. 151, they are:

Muscovite micas, including *muscovite*, $K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$, or potassium-mica, *paragonite* or sodium-mica, and *lepidolite* or lithium-potassium-mica. *Muscovite* consists of white, black, brown, yellow or green crystals, with a hardness of 2-2.5 and a specific gravity of about 2.85. It usually occurs in thin flat plates or scales. *Paragonite* is similar, but has a hardness of 2.5-3 and a specific gravity of 2.9. *Lepidolite* is of a white, grey, lilac or rose-red colour, with a hardness of 2.5-4 and a specific gravity of 2.8-2.9. Muscovite micas are fairly stable and, consequently, are often found in clays.

Biotite micas, including *biotite*, $K(Mg, Fe)_3AlSi_3O_{10}(OH)_2$, or iron-magnesium mica; *zinnwaldite*, or lithium biotite, and *phlogopite*, $AlMg_3KH_2Si_3O_{12}$, or magnesium mica. *Biotite* occurs either as scales or in large massive crystals of a black or dark green colour. In transmitted light the flakes appear brown, green or blood-red. It has a hardness of 2.5-3 and a specific gravity of 2.7-3.1. On weathering, it alters to *chlorite* and so is not often found in clays. *Zinnwaldite* is pale yellow or brown in colour (sp. gr. 2.9-3.1). *Phlogopite* occurs as white, colourless, brown or copper-red crystals or scales, with a hardness of 2.5-3 and a specific gravity of 2.75.

Hydrous micas are an alteration product of true micas from which some of the alkali ions have been leached away and more water has entered the lattice (see p. 153). They are the predominant alkali-bearing constituents of many sedimentary clays and are probably the parent of the kaolin-type clay mineral *livesite*.

Hydrous micas are often known as *illites*, and *sericites* are in this class.

Glaucinite is another variety of hydrous mica, and is a hydrated silicate or alumino-silicate of magnesium and calcium with a varying proportion of iron. It has a yellowish to blackish-green or grey-brown colour, a hardness of about 2, and a specific gravity of 2.2-2.4. It occurs chiefly in marine deposits and is a characteristic constituent of the Greensand clays and sands, to which it sometimes imparts a greenish or brown colour; on burning the colour of the glauconite is changed to that of red ferric oxide, which is characteristic of clays burned in an oxidising atmosphere.

Any kind of mica, but especially *biotite*, is objectionable in clays which are required to burn to a good white, as the iron in the mica is liable to produce a buff or brown colour. Mica frequently occurs in unaltered scales and flakes in lightly burned goods, these scales being readily recognised by their bright glistening appearance when examined by reflected light. In transmitted light, dark micas are generally citron-coloured or light-brown, whilst muscovite mica is often quite white and transparent.

Olivines are primary minerals but alter so readily that they are rarely found in natural clays. They have the composition $(MgFeCa)_2SiO_4$, and are of common occurrence in fired ceramic ware. The usual alteration product is *serpentine* in the form of *antigorite* or *chrysotile*, $3MgO \cdot 2SiO_2 \cdot 2H_2O$, which is found in some clays as predominantly green, and occasionally yellow, red, brown or almost black needle-shaped crystals with a hardness of about 3.5 and a specific gravity between 2.5 and 2.6.

The *Pyroxenes* are principally silicates of magnesium, iron and calcium with the general formula $(MgFeCa)SiO_3$. They are closely related to the *amphiboles* (see

p. 121), which are also constituents of igneous rocks. Both mineral species alter readily on weathering and yield a variety of products, chiefly *serpentine*s and *chlorite*s. Pyroxenes and amphiboles are found to a limited extent in residual clays and the principal types are:

Enstatite, MgSiO_3 , which occurs as colourless, grey, green or brown orthorhombic crystals, with a hardness of 5·5 and a specific gravity of 3·1–3·3. It is so readily decomposed that it is found only to a limited extent in clays.

Hypersthene, $(\text{FeMg})\text{SiO}_3$, forms brownish-green, green, brown or black orthorhombic crystals, with a hardness of 5–6 and a specific gravity of 3·5. It is not as readily decomposed and, consequently, is more common in some clays.

Augite, $\text{Ca}(\text{MgFe})(\text{SiO}_3)_2$ with $(\text{MgFe})(\text{AlFe})_2\text{SiO}_6$, is a silicate or aluminosilicate of calcium, magnesium and iron, which occurs in greenish-black or black monoclinic crystals, having a hardness of 5–6 and a specific gravity of 3·2–3·5. It is not easily decomposed and, consequently, is often recognised in clays.

The following pyroxenes also occur in some clays: *Bronzite*, $(\text{MgFe})\text{SiO}_3$, a silicate of magnesium and iron, *Diopside*, $\text{CaMg}(\text{SiO}_3)_2$ or $\text{Ca}(\text{MgFe})(\text{SiO}_3)_2$, a silicate of magnesium with some iron; *Diallage*, a mineral similar to diopside and augite; *Wollastonite*, CaSiO_3 , a silicate of calcium.

The *amphiboles* include *hornblende*, a variable silicate or aluminosilicate of calcium, magnesium and iron, which sometimes contains silicates and aluminosilicates of sodium and potassium; it occurs as green or black monoclinic crystals, having a hardness of 5–6 and a specific gravity of 3·0–3·47.

Glaucophane is a silicate or aluminosilicate of sodium, iron and magnesium, which occurs as bluish particles, with a hardness of 6–6·5 and a specific gravity of 3·0–3·1.

Among the less common amphiboles are *anthophyllite*, $(\text{OH})_2(\text{Mg},\text{Fe})_7\text{Si}_8\text{O}_{22}$, a silicate of magnesium and iron, *tremolite*, $(\text{OH})_2\text{Ca}_2(\text{Mg},\text{Fe})_5\text{Si}_8\text{O}_{22}$, a silicate of calcium and magnesium.

All amphiboles are readily decomposed and converted into secondary products and occur only in small proportions in clays.

Pyroxenes and amphiboles are not usually present in clays in quantities sufficient to influence the properties. They would tend to discolour fired ware, act as slow fluxes, and reduce the refractoriness.

Tourmaline is an accessory mineral in many granites and as it is very stable, it is a common constituent of many crude china clays where it may be recognised in the form of blue needles. It is an aluminium borosilicate or a boroaluminosilicate which occurs as black or blue-black hexagonal crystals, with a hardness of 7·0–7·5 and a specific gravity of 2·98–3·2.

SECONDARY MINERALS IN CLAYS

Secondary minerals are of much more common occurrence in clays and they include the clay minerals, of the kaolin and montmorillonite group, chlorites, vermiculites and hydrous micas.

The principal minerals of granitic igneous rocks, which break down under the action of natural agencies are the feldspars and micas. In the presence of weak acids

(e.g. carbonic, boric), feldspar changes to kaolin-type minerals. The micas give a variety of products, depending upon their composition; muscovite mica yields hydrous mica and, finally, the kaolin mineral, livesite; biotite micas change to chlorites or vermiculites and it is speculated that kaolin minerals may be the end product.

The general alteration reactions under alkaline conditions and the products from basic igneous rocks, e.g. basalts, give different products from those formed through the medium of acids. Rocks rich in ferro-magnesian minerals are the principal sources of the montmorillonite minerals; the olivines, pyroxenes and amphiboles transform through a variety of intermediate forms and the final product depends to a great extent on the composition of the original minerals. Montmorillonite minerals may also be formed by crystallisation from solutions containing aluminium, silicon, magnesium and iron, and also by the co-precipitation of gels of the hydroxides of those elements.

Kaolin minerals of composition $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ are the most prevalent mineral group found in natural clays, although hydrous mica or illite is also common. The mineral, *kaolinite*, is not of frequent occurrence and may be restricted to those clays which have been formed under hypogenic action, i.e. sub-surface reaction at high temperatures and pressures (e.g. china clay) and to the direct sediments of those clays (e.g. ball clays).

Halloysite forms under conditions of strong acid attack (e.g. sulphuric and sulphates) in the region of mineral springs or intense volcanic activity. *Nacrite* and *dickite*, the most well-formed of all kaolin minerals, have probably crystallised from solution under specific acid conditions. The latter mineral is occasionally associated with nodular ironstone in fireclay seams.

The most common clay mineral in sedimentary clays is *livesite*, which has a fine grain size. It may be derived from a micaceous component (see Chapter III) and have a small proportion of cations, other than aluminium or silicon as part of its lattice.

Allophane is another kaolin type mineral but of variable composition. It is not of common occurrence.

Montmorillonite minerals are less common than kaolins, but numerous examples are known. They are of variable chemical composition containing aluminium, silicon, magnesium, iron and other elements. *Montmorillonite*, *beidellite* and *nontronite* form one series of minerals where silica, alumina, magnesia, iron oxide and water are the principal components. *Saponite* and *hectorite* are other types of montmorillonite containing chiefly magnesia, lithia, silica and water. The general name given to clays which contain appreciable quantities of montmorillonite minerals is *bentonite*.

Attapulgit or **palygorskite** is another secondary mineral present in some clays. It is not of common occurrence, but, in a pure state, it is particularly valuable for drilling fluids and as a filler. It is essentially a hydrated magnesium silicate, but other elements may be present.

Chlorites are a group of hydrous aluminosilicates with iron and magnesium as essential ingredients; they occur as greenish flakes resembling mica. They have a hardness of 1.5 and a specific gravity of 2.5–2.8. Chlorites are the most usual

alteration products in recent clays derived from minerals rich in magnesium and iron and they are common constituents in many sedimentary clays.

Vermiculites are not uncommon in clays of recent origin. They are hydrated magnesium silicates but other elements, chiefly iron, are frequently associated. They owe their name to their property of exfoliating on heating. They occur as plate-like flakes, are softer than mica and are usually red, brown or black.

Epidote, $4\text{CaO} \cdot (\text{AlFe})_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot \text{H}_2\text{O}$, forms a group of aluminosilicates of iron and calcium, with sometimes manganese and cerium, etc. It occurs as green or brownish, monoclinic, lath-shaped crystals with a hardness of 6-7 and a specific gravity of 3.37-3.50. It is an alteration product of ferromagnesium minerals and iron-bearing feldspars.

Clay minerals usually impart plasticity to clays; montmorillonite is extremely plastic and sticky, kaolin types less so, and chlorites and vermiculites not at all. Kaolin minerals are the most refractory because they are essentially aluminosilicates and contain far less fluxing elements than the other types. Kaolin minerals are white burning (except livesite) and are common constituents of whiteware bodies. The principal properties of clay minerals are summarised in Table VI.I.

TABLE VI—I. SOME PROPERTIES OF CLAY MINERALS

	<i>Kaolin</i>	<i>Montmorillonite</i>	<i>Chlorites, Vermiculites, Hydrous micas</i>
Particle size	Small	Extremely small	Variable, but comparatively large
Plasticity	Good	Very good	Poor
Fired colour	White (mostly)	Cream, buff or red	Brown, red or black
Refractoriness	1710° C.	1350-1450° C.	1250-1500° C.

Clay minerals are difficult to detect because they are usually of small particle size. Chlorites, vermiculites and hydrous micas are frequently of a sufficiently large size to be identified by the optical microscope; kaolins are readily observed under the electron microscope, but montmorillonites are not easily discerned. Differential thermal analysis affords a simple and effective method of detecting and estimating many of the clay minerals, from the nature and temperature of the characteristic peak or peaks corresponding to the loss of structural water. The main clay mineral groups can be differentiated by X-ray analysis and most individual types are recognised.

Another class of minerals which occurs in many clays and has an important bearing on some of their properties is referred to as **organic or carbonaceous matter**; it is present in variable proportions according to the mode of formation and the conditions to which the clays have been exposed. It is derived chiefly from (a) the percolation of water containing humic acids and matter in solution or suspension, the organic matter being absorbed by the pores of the clay and so retained; (b) the deposition of clay upon organic matter or the deposition of organic matter on clay beds, the carbonaceous material being gradually incorporated into the clay; or (c) the admixture of bituminous or carbonaceous rocks with the clay during the deposition of the latter.

The carbonaceous matter may be disseminated either in large masses, minute grains, or as films over the surfaces of the other grains. Ball clays usually contain 3–4 per cent, and sometimes as much as 10 per cent of carbon in the form of an organic jelly derived from peat, lignite, coal or other organic matter—usually of vegetable origin—or in the form of oleaginous matter derived from fossilised fishes and creatures having shells, which, on heating, produce 'shale oil' and give them a dark colour. Sometimes the plants from which the organic matter has been derived may be identified but the greater part of it has usually decomposed too much to be definitely recognisable. All the organic carbon present in a clay may be burnt off when the clay is heated to redness in a current of air, but the process requires care, or the mass may be bloated and superficially fused in such a manner as to prevent the oxidation of all the carbon.

In primary clays, such as *china clays* and *kaolins*, organic matter is practically absent; it is most abundant in plastic clays, such as those used for the manufacture of bricks, tiles, terra-cotta, etc.

The **chief effects of carbonaceous matter** are (i) it imparts a dark colour to the raw material (p. 816), (ii) it may produce reducing conditions during kiln firing and so affect the colour and the vitrification behaviour, (iii) it may reduce the amount of fuel required for burning the clay, (iv) it may burn too rapidly in the kiln and cause over-vitrification and loss of shape, (v) it may give rise to a 'black-heart'.

Carbonaceous matter is sometimes deliberately added to a clay to produce desirable effects: (a) large particles of coal (up to pea-size) provide localised reducing conditions and, in some clays, give a pleasing appearance to the outside of facing bricks made from them—about 5 per cent of coal by weight is normally added; and (b) finely-divided breeze incorporated into a clay can provide sufficient heat on controlled burning to burn bricks completely without the need for additional fuel. This is the usual procedure in *clamp-firing*, where about 15 per cent of combustible is used—bricks of excellent colours are thereby produced if the clays have a sufficient proportion of iron compounds.

The presence of a proportion of low-rank carbonaceous matter, e.g. algae or oily constituents, is an advantage in some clays, because if the firing is carefully controlled, the organic components decompose steadily over a wide temperature range, thereby reducing the total fuel required and giving a more uniformly-fired brick.

High-rank carbonaceous matter, e.g. bituminous and anthracitic coals, is not so desirable in clays, because it commences to burn only at high temperatures and then very rapidly, so that ware containing it tends to become over-vitrified.

If the carbonaceous matter is in the form of fine grains uniformly disseminated through the clay, it is not usually harmful, and is readily burnt out by slowly heating the clay in an oxidising atmosphere, care being taken to avoid surface fusion which seals the pores and prevents all the organic matter from being fully oxidised. Where larger masses of organic matter occur, however, it may cause trouble because of the amount of heat and gas evolved, causing superficial fusion, and because of the large cavities which are left when the particles of organic matter have been burned away. In all cases where a clay contains sufficient organic matter especially of a coaly or graphitic nature and sufficient fluxing materials, such as lime or soda compounds, the

firing process is difficult to control and often results in the production of 'black hearts', and sometimes of a highly bloated mass. These objectionable changes are due to the fact that the very close texture of some clays prevents the ready access of air to the interior of the articles. If much carbonaceous matter is present, before it can be oxidised and removed, the exterior pores of the article become closed with fused material and so effectually prevent the removal of the carbonaceous matter. Unless great care is taken to control the rate of combustion and the rise in the temperature of the mass, superficial fusion may occur, and if this takes place sufficiently, it will be impossible to remove the black 'core' or to reduce the swelling by any treatment which does not spoil the ware.

Water may also be conveniently regarded as a mineral and it is present in clays in a variety of forms. These are:

(a) *Hygroscopic water* or *moisture*, the amount of which depends on the surface area of the clay.

(b) *Absorbed water*, which is associated with the exchangeable cations in certain clay minerals.

(c) *Broken-bond water*, which is linked to the unsatisfied valencies occurring at the edges of crystals, and

(d) *Combined water* or *water of constitution*, an essential part of the structure of some minerals.

The various forms of water are described in Chapter VIII.

Exchangeable Cations. In addition to the elements which form part of their crystal structure, some minerals can absorb cations (or bases) from solutions. Clay minerals have this property to a marked degree; montmorillonite, for example, may have up to 3 per cent by weight of sodium or calcium oxide retained in this way. Kaolinite does not usually absorb more than 0.3 per cent, but livesite may contain up to 1.0 per cent.

The cations absorbed are many, but hydrogen, sodium, potassium, calcium and magnesium predominate, although aluminium and iron are common in some clays. Only small-sized minerals have the capacity for cation absorption, and it is probably due to a charge deficiency on the particles. Although the cations are closely associated with the mineral crystallites, they may be readily exchanged by others under suitable conditions—hence the property is known as the *cation-exchange capacity*. It is considered in more detail in Chapter V (p. 264), where methods for its measurement are outlined.

The type of cations which are present in natural clays depends principally on the mode of formation and the environment. Clays associated with lime strata, for example, will contain principally calcium ions; those derived from rocks containing alkali have predominantly sodium or potassium ions; in clays which have been extensively leached or weathered, the exchangeable ions are chiefly hydrogen.

The properties of the clay may be greatly influenced by the type of associated cation. The behaviour of clay in water is most markedly changed when cations of different types are present (see Chapter VIII). The exchangeable cations may influence the plasticity, drying shrinkage and firing properties of clays if they are present in appreciable quantities.

THE VARIETIES OF CLAYS AND THEIR COMPOSITION

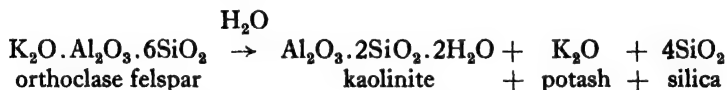
THE materials known as *clays*¹ differ so greatly in composition and properties that it is impracticable to class them accurately and in great detail. The following are some of the best-known and widely-used clays; other clays of geological or mineralogical interest but of no commercial importance are not included, though they may be used locally in small quantities for making bricks, roofing tiles and crude earthenware vessels.

All clays are composed of (a) one or more clay minerals, and (b) other minerals, the proportions of each being varied according to the origin and subsequent (natural) treatment of the clay.

In most materials described as clays, the *clay minerals* are the predominant and essential constituent, and this should always be borne in mind though in some commercially-useful brick- and tile-clays the total clay minerals may be only 30–35 per cent of the whole material, and in some workable clay-pastes it is even less. For more than a century, the existence of some essential *clay-substance* has been assumed, though the recognition of definite 'clay minerals' with a distinct individual crystalline structure has been established only within the last 30–35 years. The lattice structures of the clay minerals are described in Chapter III and the other minerals are described in Chapter IV.

China Clays. *China clays* and *kaolins* are mainly residual clays, formed *in situ*, by the breakdown of primary minerals. The principal deposits of this type of clay are the result of hydrothermal reactions in large granitic masses, and the resulting *kaolinisation* is found to great depths in some igneous rocks.

The principal mineral which undergoes alteration is the felspar component which loses its alkali and some of its silica and gains water of constitution. The reaction may be represented simply by:



The alkali is usually removed as a soluble salt.

The true nature of the reaction is not fully understood; several intermediate stages may form before the final product is reached.

In the Cornish granites the reaction has probably proceeded through the agency of water containing free acids (such as hydrofluoric, hydro-boric and carbonic) at high temperatures and under great pressures, the solutions having been forced up from below and penetrating the granite through fissures and jointings. As the felspar breaks down the granite mass becomes porous and more powdery and yields

¹ Many clays have names which are likely to cause confusion—particularly in the United States and Germany. The fact that a clay bears an English place-name does not necessarily mean that it is found in England. Several such clays occur only in the United States and the place-name is often a trade-name. Many clays are named after a mineral species which they contain; others, after the type or character of the clay, e.g. flint clays; some are called by a name intended to indicate the use of the clay, e.g. pot-clays.

Much of the confusion which exists in clay terminology has been outlined by Robertson and his survey of existing trade-names greatly clarifies the position. (Robertson, R. H. S., *A Glossary of Trade Names* (Mineralogical Society, London, 1954)).

what is termed *china-clay rock* or *carclaxite*. This material varies greatly and contains only about 20 per cent of kaolinite on the average, the remainder consists of unchanged quartz, mica and other primary minerals, including some unaltered feldspar. It is a curious fact that, broadly speaking, the greater the depth at which the altered rock occurs, the richer is the material in kaolinite.

The complexity of the decomposition and other changes is great, because in addition to (i) *kaolinisation*, two other alteration processes are recognisable in the Cornish granite; (ii) *tourmalinisation* which occurs in regions where the ascending solutions, rich in boron, have converted the micaceous and feldspathic constituents into tourmaline (p. 287), and (iii) *greisenisation* or a process of alteration mainly involving solutions containing fluorine; the feldspars break down forming quartz and hydrous mica; topaz $(\text{AlF})_2\text{SiO}_4$ and fluorite (CaF_2) may also be present. The three processes are often superimposed so that the resulting china-clay rock may have a complex composition.

Fortunately, the kaolinite produced consists essentially of much smaller particles than most of the associated minerals and, as a result, it can be concentrated by a process in which the clay mineral is extracted with jets of water or steam; the slurry so formed flows to the foot of the quarry-face and settles in large tanks. Most of the coarsely-grained quartz, unchanged feldspar, mica and other components are thus removed and the purified kaolinite extracted by evaporation or by filter-pressing.

The theory that kaolinisation is the result of the action of ascending hot acidic solutions is widely accepted to explain the origin of the Cornish china clay and similar deposits in France and Germany. However, kaolinite may also be produced from feldspar under normal atmospheric weathering conditions and some American, Asiatic and possibly some European kaolins may have been formed in this way. Such kaolin deposits differ in thickness and texture from those of hypogenic origin.

True kaolinite deposits are not as widely spread as was formerly thought. The only ones of any economic importance are those where a large mass of igneous rock has been altered by hydrothermal action, as in Cornwall and Devon, Ayrshire, the Massif Central in France, Saxony and Bavaria in Germany, Czechoslovakia, China, Australia and in a few localities in the Americas particularly North Carolina.

The best kaolins for refractory and ceramic use are those purified from residual deposits. Sedimentary or re-deposited kaolins are found in the United States and elsewhere and are of economic value, but they are not as pure as kaolin prepared from china-clay rock.

Kaolinite, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, when pure, has the composition (by weight) alumina 39.56 per cent, silica 46.54 per cent, water 13.90 per cent. Commercial kaolins contain between 80–90 per cent of the clay mineral, contaminated mainly with quartz and fine-grained mica or hydrous micas but seldom with appreciable proportions of feldspar. As the particle-size distribution of all the minerals present is similar, it is difficult to deduce a mineralogical analysis with much degree of accuracy. An analysis of a purified sample of Cornwall china-clay is shown in Table VI.II. From this, if an average value for a mica component is accepted, a mineral balance sheet can be computed. An accurate estimate of the kaolinite content can also be secured by thermal analysis. In this sample, the free silica content was exceptionally

low and only a trace was revealed by X-ray methods. The amounts of other minerals detected by microscopic and X-ray methods have to be inferred from the chemical analysis.

TABLE VI—II. MINERALOGICAL BALANCE OF A CORNISH CHINA CLAY

<i>Mineral</i>	<i>Per cent</i>	<i>SiO₂</i>	<i>Al₂O₃</i>	<i>TiO₂</i>	<i>Fe₂O₃</i>	<i>CaO</i>	<i>MgO</i>	<i>K₂O</i>	<i>Na₂O</i>	<i>Loss on ignition</i>
Kaolinite	89.00	41.44	35.13							12.43
Mica	7.10	3.24	2.75					0.58	0.18	0.35
Quartz	2.04									
Goethite (FeO. OH)	0.91				0.69					0.22
Sphene	0.09			0.09						
Fluorite (CaF ₂)	0.55					0.28				0.27
Tourmaline	Trace									
Mg mineral	Trace									
Total	99.69	46.72	37.88	0.09	0.69	0.28	—	0.58	0.18	13.27
Actual chemical analysis	100.04	46.72	37.88	0.09	0.69	0.28	0.24	0.58	0.18	13.38

Other kaolinites show similar results on analysis although they usually contain a greater proportion of impurities. One important point emerges from the mineralogical analysis which cannot be stressed too strongly. It is that the total amount of impurity (i.e. oxides other than alumina and silica) in the kaolinite total only 2.06 per cent, but when this is calculated on a mineralogical basis the non-kaolinitic material is as high as 11.0 per cent principally due to the proportion of silica and alumina in mica.

Pure kaolin or china clay is white-burning and has a refractoriness of about 1785° C., although if much impurity is present the softening temperature will be reduced. Kaolins which have been formed by surface weathering agents invariably contain a higher proportion of iron-bearing minerals than those formed by hydrothermal actions. Such clays tend to burn brown, red or pink on firing and are not as valuable for some ceramic purposes.

Halloysite-bearing Clays. Clays which contain the clay mineral *halloysite* resemble the china clays in appearance and in some properties, but are more plastic and produce a denser fired body. No halloysite-bearing clays are definitely known in the British Isles although some authorities claim that this mineral is present in fireclay in the Glenboig district in Scotland.

Halloysite probably has a similar origin to kaolinite but the hydrothermal agents were more acidic and may have contained sulphate or chloride radicles. The fact that *alunite* (K₂O. 3Al₂O₃. 4SO₃. 6H₂O) is commonly associated with halloysite clays strongly supports this theory. Ross and Kerr¹ consider that some halloysites may be a crystallisation product from solutions or derived from allophane or diaspore, for those minerals are also frequently present. There is geological evidence which suggests that, under favourable conditions, halloysite may recrystallise and form kaolinite and an example of the reverse change is to be found in the halloysites

¹ Ross, C. S. and Kerr, P. F., *U.S. Geol. Survey Prof. Paper*, 185-G, 135, 1934.

at Cadouin in France, where kaolinite is altered to halloysite in the region of mineral springs, rich in sulphate.

Halloysite is a common constituent of some American flint clays, particularly in Utah and Indiana where it is found in both the normal and hydrated form. An exceptionally pure sample was worked at Angleur, near Liège in Belgium, but this supply has apparently now been exhausted.

Steinmark or *Lithomarge* is sometimes regarded as 'a variety of china clay'. It is a white or cream-coloured material, somewhat dense and coherent, but not very plastic; it is converted by hydrochloric acid into a white glistening mass. According to Ross and Kerr¹ lithomarge is a mixture in part at least of kaolinite and halloysite. Its composition appears to vary greatly, and an average composition for this material seems to be 47 per cent of silica, 39 per cent of alumina, and 14 per cent of water, but Bischof has found some samples with as high a proportion of alumina as 41·48 per cent, and classed it with the bauxites rather than with the clays. Its unctuous feel, slight though distinct plasticity and its general physical nature suggest, however, that it is closely allied to clays.

Its origin is uncertain, though the best specimens are found in association with the Bunter sandstones, particularly in Germany. It is, however, impossible to allocate it to any single geological period. Indeed, the term 'lithomarge' is applied to so wide a range of materials that it is almost as indefinite in meaning as the terms 'pipeclay' or 'fullers' earth'.

Myelite is regarded as a white, conchoidal variety of lithomarge, and *carnalite* as a pink and more compact form. *Tuesite* is a bluish variety found at the mouth of the Tweed.

Other minerals similar to clay, but much contaminated by other substances, also occur. Thus *bole*, *umber*, and *sienna* consist of ferruginous clayey material of a brownish-yellow or red colour and of very variable composition. When these various minerals are heated they behave in a manner similar to clay, though the other minerals usually present as impurities enter into combination with them and their decomposition products, and so produce so complex a mixture that it is almost impossible to ascertain its mineralogical composition.

Ball Clays. Clays which are plastic or 'sticky' yet burn white, are termed *ball clays*. They are of value because they can be added to true china clays to give strength to the moulded shape and yet maintain the white colour after firing. One essential feature of ball clays is their fine grain size (much less than that of china clay) which is the main reason for the high plasticity.

Large deposits of ball clays occur in the south-western counties of England, and they are widely used in the British Isles particularly in the white-ware industry. The three important producing areas are in Dorset, North Devon and South Devon.

Unlike the residual true kaolins, ball clays are sedimentary in character, i.e. they have been transported by rivers and deposited at some place removed from the site of formation. The English ball clays were most likely formed in the Cornwall granite mass, and afterwards removed by rain, carried by rivers and probably deposited in fresh water lakes at a time when the coast-line was very different from

¹ Ross, C. S. and Kerr, P. F., *U.S. Geol. Survey Prof. Paper*, 165-E, 175, 1931.

that of the present day. Scott¹ has suggested that the Dorset deposits were laid down in the Miocene period of the Tertiary era of geological formation (see p. 44) and those of Devon at a later period. It is probably more correct to ascribe the Dorset beds to an earlier epoch, as the fossil remains resemble those in the Brown Coal deposits of Germany which belong to the Oligocene period.

Although ball clays are undoubtedly fresh-water deposits, the diverse nature of some of them suggests that they are, in part at least, of fluvatile origin. High-quality clays are usually found in small pockets associated with lignite and coarse-particled gravels.

The South Devon deposits, which occur in the vicinity of Bovey Tracey and Newton Abbot, are truly lacustrine. These clays are fairly well bedded and although there is much associated lignite and gravel, they can be worked either by open pit or underground mining methods. The beds are characteristically lenticular and there is a complicated sequence of clay, lignite and gravel which in some places is known to extend to depths of 1000 feet.

There is considerable support for the theory that the ball clays are derived from the Cornwall granite, for in the South Devon deposits there is a tendency for the clays to become finer towards the more eastern edge of the area. This would represent the position of maximum transportation if the source were centred in Cornwall.

Ball clays are invariably dark in colour, due to associated lignite, but in those of the best quality this readily burns away and produces a white body; others are suitable for coloured ware, stoneware or other purposes. Some gravel and sand occur in the clays, but can usually be removed by blunging with water and sieving or allowing the coarser particles to settle and pumping off the 'fines' in suspension.

The lignite and gravel contamination is a result of the frequently changing conditions whilst the clays were being transported and deposited. Some other minerals present in the primary rock have been transported along with the clay itself and are of comparable grain size; they form a part of the impurities in the ball clays. *Hydrous mica* or *sericite* is usually the commonest accessory mineral and as it is of similar particle size to that of the kaolin mineral itself, it is difficult to remove. Ball clays invariably contain a larger percentage of impurities than purified china-clays, and so have a lower refractoriness. They tend to shrink appreciably on firing and produce a denser body.

The ball clays from South Devon localities are composed chiefly of the clay mineral *kaolinite*, but the particle size of this mineral is much less than in china-clay. Some of the Dorset clays appear to contain a kaolin mineral more closely related to *livesite*. A sample from the vicinity of Torrington in North Devon contained a clay mineral of the *livesite* type and was rather richer in iron than those from South Devon. It may have resulted from surface weathering and not be of true hydrothermal origin.

The difference in clay mineral type does not seriously influence the properties of the ball clays. Both *kaolinite* and *livesite* have the same chemical composition although the latter has inherently a finer grain size, which for the same content of clay mineral should make it more plastic.

¹ Scott, A., *Memoirs of the Geological Survey*, vol. 31 ('Ball Clays', H.M. Stationery Office, 1929).

Ball clays are found in other countries but they are not of common occurrence and few are of such good quality as the British material.

Chemical analyses of ball clays show that they are richer in silica than china-clays and there is a correspondingly smaller alumina figure. They usually contain more alkalis, iron oxide and carbonaceous material. The percentage composition figures vary considerably, but usually fall within the following limits:

Silica	45-60 per cent
Alumina	25-35 per cent
Loss on ignition	7-15 per cent
Iron oxide	less than 2 per cent
Lime and Magnesia	less than 1 per cent
Potash and Soda	less than 3 per cent.

The mineralogical composition is also very variable but the three main components are always the clay mineral (either kaolinite or livesite), hydrous mica and quartz with some primary mica and titania, but no felspar. The carbonaceous material in ball clays is present in a finely-divided state (probably in colloidal form) surrounding grains of other minerals; it is possible that the plasticity of the clay is thereby increased.

The compositions of many ball clays from Devon and Dorset have been investigated by Holdridge.¹ He found that the essential mineral components were kaolinite (in Dorset samples it was a 'disordered' form), quartz, mica, organic matter with TiO_2 present as anatase. He calculated the mineralogical composition by means of 'rational analysis' (see p. 217) and by assuming that the principal alkali-bearing mineral was mica, he concluded that the range of mineral contents in the important British ball clay areas was as given in Table VI.III.

TABLE VI—III. MINERALOGICAL COMPOSITION OF
BALL CLAYS
(after Holdridge)

	<i>North Devon</i>	<i>South Devon</i>	<i>Dorset</i>
Kaolin-type	33-68 per cent	20-90 per cent	20-83 per cent
Quartz	15-48 per cent	0-60 per cent	5-60 per cent
Mica	0-22 per cent	0-40 per cent	0-30 per cent
Organic Matter	0-3 per cent	0-16 per cent	0-8 per cent

This table includes the siliceous ball clays which have a total silica content of 60-80 per cent, due to a higher content of quartz than is usual.

It is evident from the manner of their formation and subsequent transportations and depositions, that the composition of ball clays must depend largely on that of the original altered rock and almost equally on the accidental impurities which have been mixed with them. In all ball clay pits, there is a great variety of clays, differing considerably from each other, so that it is necessary to exercise skill and care in excavating and in keeping the various grades separate. Serious losses in spoiled ware may occur if ball clay from another source or, sometimes from another seam in the same area, is substituted without the possible effects of the change being realised.

¹ Holdridge, D. A., *Trans. Brit. Ceram. Soc.*, 55, 359, 1956.

Changes in the physical properties of a ball clay are often quite as serious in their effects as changes in the chemical composition.

Much importance is attached to the smallness of the grain-size and the best clays are expected to contain 80 per cent of particles less than 0.001 mm., with 50 per cent between 0.0002 mm. and 0.0006 mm.

Ball clays are found in other countries, but are not of common occurrence. In the U.S.A., the chief producing areas are Tennessee and Kentucky, where the clays are similar in composition and property to those of Devon and Dorset.

The chief uses of ball clays are to increase the plasticity of other white-burning clays, flint, etc., in the manufacture of whiteware bodies. They are important ingredients of engobes, dips and spray-slips and are used in the manufacture of abrasive wheels, insulators and moulding sands. Some of the cheapest ball clays are used as *fillers* in the rubber, paint and plastics industries.

Refractory Clays. Refractory clays are those with a high resistance to heat without loss of shape. This group includes many clays, but the most important are the fireclays.

Fireclays are clays which have a high refractoriness and although there is no definite stipulated lower temperature limit, a softening point of 1500° C. is usually regarded as a minimum and one greater than 1600° C. is generally required. Fireclays are widely distributed and are of many types, the principal of which are (a) *flint clays*, where the clay material has been compacted by pressure of overlying strata into a dense, hard, rock-like mass; (b) *plastic clays* which are much softer and are readily broken down by water into a mouldable mass of high plasticity, and (c) *shales* where a refractory clay has again been compacted by pressure, in such a manner that the mass readily cleaves along well-defined planes.

The important fireclay deposits¹ in the British Isles are associated with the Coal Measures which were laid down in the Carboniferous era of geological deposition. They are the oldest clay deposits which are worked on an extensive scale in this country. In the course of geological time, further deposition has taken place and the weight of this overlying strata has compressed the Coal Measure clays into narrow bands or beds of extremely hard material.

The associated coal seams appear to play a considerable part in determining the refractory nature of the clay, as good quality clays accompany coal and lignites laid down in other geological periods. The carbonaceous material usually overlies the clay seams and the vegetation from which the coal is derived may, whilst growing, have extracted alkalies and other impurities from the clay (soil), thereby increasing its refractoriness. At a later stage, the decaying vegetation may have bleached the clay and rendered the iron soluble and so removed it.

The conditions under which the Coal Measure fireclays were formed is not known with certainty, but it is likely that the sediments were carried by large rivers from a vast land mass which extended from Greenland to Northern Scandinavia. Deposition took place over a large area, in conditions which resemble fresh water rather than marine formation.²

¹ Some refractory clays at Ewell, Surrey, have long been used to make fireclay bricks, though they are not obtained from the Coal Measures.

² Similar conditions but on a smaller scale are to be found at the present day at the mouth of the Amazon where the water is comparatively fresh to a distance of over 300 miles into the Atlantic.

The formation of the Coal Measures extended over approximately 80 million years (see table, p. 45) and, during the period, frequent land movements took place which changed the level of the bed and altered the conditions of deposition. Swampy, deltaic, lacustrine and sometimes marine conditions followed, sometimes in regular sequence, giving rise to coal seams, sandstones and gritstones, fireclays and shell bands.

Coal Measure fireclays occur in many localities in the British Isles and abroad. They are worked wherever valuable seams outcrop, and important producing areas in Great Britain are the Central Lowlands of Scotland, Northumberland and Durham, West and South Yorkshire, Cumberland, parts of Lancashire, Staffordshire, Shropshire, North and South Wales and parts of South-west England. The outcropping seams in each locality are usually different, and a productive seam in one area may be of no value in another. The measures may vary in thickness from a few inches to several feet and only a limited number can be worked profitably. The usual methods of winning are by drift mining, by outcrop quarrying and by deep mine workings.

The clay seams vary considerably in composition and properties and there is no progressive relationship to geological age. In addition, clays extracted from one particular seam, but at different points along it, may show considerable variations.

Fireclays are the most extensively used refractory material and the nature of the minerals present in them and their influence on the property of the fired bricks have been the subject of much research for many years.

The behaviour of a clay at high temperatures is entirely dependent on the minerals which are present and on their grain-size distribution. This is well-illustrated by the fireclays, so that a chemical analysis can, at the most, give only the first indication of the value of a clay as a refractory material. Considerable variation in chemical composition is found in fireclays from different sources, the range of composition being:

Silica	40-80 per cent
Alumina	10-40 per cent
Loss on ignition	5-14 per cent
Iron oxide	1-5 per cent
Lime	} Less than 5 per cent
Magnesia	
Alkalies	Less than 3 per cent
(low-grade samples may have up to 4 per cent)	

In general, the higher the alumina content of a fireclay, the greater is the refractoriness. Chemical analyses of fireclays from the principal British localities are shown in Table VI.IV, but these may not be typical of the locality, particularly where more than one seam is worked.

The results given in Table VI.IV are the analyses of the most productive seams in each locality, but do not include minor workings, where clays with analyses outside the stated limits may be produced.

The wide range of composition in clays from each area is to be expected because numerous seams are mined which have very different characteristics. In the

TABLE VI—IV. CHEMICAL ANALYSES OF FIRECLAYS FROM THE MAIN PRODUCING AREAS

	Cumberland		Derbyshire and Warwickshire		Durham and Northumberland		Lancashire and Cheshire		North Wales	
	Range	Average	Range	Average	Range	Average	Range	Average	Range	Average
SiO ₂	45-69	57.5	46-70	56.0	48-65	57.0	45-70	57.5	43-78	63.0
Al ₂ O ₃	22-36	26.5	18-41	27.5	22-37	27.0	18-36	25.0	15-37	22.5
Fe ₂ O ₃	1.2-2.9	2.0	0.1-2.8	1.7	1.1-2.1	1.6	1.1-7.0	3.6	1.0-8.0	3.3
TiO ₂	0.8-2.2	1.2	0.9-2.7	1.3	1.0-1.3	1.1	0.8-1.5	1.1	1.1-1.5	1.3
CaO	0.2-0.4	0.3	0.2-0.7	0.4	0.1-0.3	0.2	0.1-0.8	0.4	0.2-1.4	0.5
MgO	0.4-1.0	0.6	0.0-0.8	0.6	0.5-1.1	0.7	0.5-1.8	1.1	0.1-1.4	0.7
Na ₂ O	0.2-0.4	0.3	0.2-0.6	0.4	0.0-0.3	0.1	0.0-0.4	0.2	0.1-0.3	0.2
K ₂ O	1.0-4.3	2.4	0.8-3.3	2.4	1.3-4.5	2.2	0.4-3.9	2.2	0.8-3.4	1.8
Loss on ignition	7-15	9.0	7-14	9.5	9-12	10.4	7-14	9.6	5-12	7.5

TABLE VI—IV. CHEMICAL ANALYSES OF FIRECLAYS FROM THE MAIN PRODUCING AREAS

	South Wales		Scotland		Staffordshire, Worcestershire, Shropshire		Yorkshire	
	Range	Average	Range	Average	Range	Average	Range	Average
SiO ₂	53-76	64.0	31-64	50.5	43-74	59.0	44-72	58.0
Al ₂ O ₃	12-28	21.5	25-52	34.0	13-36	25.0	19-43	25.5
Fe ₂ O ₃	0.6-6.3	2.6	0.5-6.4	2.3	1.0-3.3	2.1	1.0-4.0	2.2
TiO ₂	0.9-1.4	1.1	1.0-4.3	1.7	0.5-1.7	1.1	1.0-2.3	1.5
CaO	0.1-1.5	0.5	0.1-1.0	0.4	0.0-0.6	0.3	0.1-0.5	0.3
MgO	0.2-1.2	0.7	0.1-1.2	0.5	0.1-0.9	0.4	0.0-1.5	0.7
Na ₂ O	0.0-0.5	0.2	0.0-0.8	0.2	0.0-0.7	0.2	0.0-0.8	0.3
K ₂ O	1.7-3.4	2.1	0.2-1.9	0.7	0.1-2.2	1.1	0.4-1.5	1.8
Loss on ignition	5-11	7.2	7-20	11.2	6-19	9.9	7-16	10.3

Yorkshire area, for example, clays range from those of the Lower Coal Measures to Middle and even Upper Coal Measure strata.

In general, however, the fireclays with the highest alumina contents are found in Scotland; North and South Wales deposits are less refractory, on the average, than those from the other producing areas.

The figures for the average analyses of fireclays from each area are the statistical mean of many samples. Of especial interest are:

- (a) the small but fairly constant proportion of titanium dioxide;
- (b) the ratio of magnesia to lime which is always about 2:1, but the total amount of alkaline earth oxides rarely exceeds 1.5 per cent of the whole;
- (c) the content of alkalis (i.e. sodium and potassium oxides) usually lies between 1.3 and 3.0 per cent in the refractory clays, but in all cases the proportion of potassium to sodium oxide is between 6 and 10 to 1;
- (d) the loss on ignition figures include carbonaceous material in addition to water of constitution. In some samples, the organic matter amounted to 10 per cent by weight.

Grimshaw, Carr and Roberts¹ have deduced the mineralogical composition of several fireclays in the Yorkshire area. This work has been extended and samples from many British localities have been analysed by standard methods. Although there is considerable diversity in chemical composition among the clays examined, the minerals present in all the samples are similar; it may be concluded that all the fireclays differ only in the relative amounts and grain size of three main constituents.

Each clay examined was analysed by the standard procedures described in Chapter V. The clays were broken down in water and then separated into grain size ranges by sieving, followed by sedimentation, and the final fine fractions were obtained by centrifuging.

Some clays contained particles which were of coarse grain; this was particularly so in the case of the micaceous component and sand where in some fireclays, large flakes were retained in the sieves.

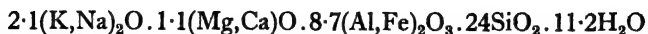
Further treatment of the various grain size fractions enabled all the minerals present to be isolated. Of all clays examined three minerals were common to all, and together these amount to more than 90 per cent of the total clay. These minerals are:

(a) *Free silica* or *sandstone*, which, in most clays, is comparatively coarse-grained (upwards of 10μ). It has a high content of total silica which, in many samples, is largely crystalline quartz, although some flint or chalcedonic particles have been identified under the microscope. The content of this sandy component is variable, ranging from 0 to as much as 50 per cent in some samples. All fireclays which have a high total silica content on analysis are rich in free silica.

(b) A *clay mineral* of the kaolin group which, in all samples so far examined, has been *livesite* (see p. 134). This mineral has the composition $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, and is inherently so finely grained that it imparts plasticity to the clay. The content of livesite in fireclays is again variable, but is rarely less than 15 per cent.

¹ Grimshaw, R. W., Carr, K. and Roberts, A. L., *Trans. Brit. Ceram. Soc.*, 51, 334, 1952.

(c) A *micaceous mineral*, which is classed as a hydrous mica because it contains less potash and more water of constitution than true muscovite (see p. 153). This mineral is of variable composition and is, therefore, difficult to estimate in clays, especially when it is present in fine grain-sizes. An average molecular composition of the micaceous component is



(cf. muscovite mica $4\text{K}_2\text{O}\cdot12\text{Al}_2\text{O}_3\cdot24\text{SiO}_2\cdot8\text{H}_2\text{O}$), but in deriving a mineralogical balance of a particular clay it is advisable to isolate a pure sample for analysis. Hydrous mica is the principal alkali-bearing mineral in fireclays, and in many other sedimentary clays.

Some idea of the total amount of hydrous mica in a clay is shown by the total alkali figure, determined by chemical means, after first deducting the exchangeable bases in the clay. In the average hydrous mica, the alkali content is about 6·7 per cent, therefore a clay with 2 per cent total alkali may contain as much as

$$\frac{2 \times 100}{6\cdot7} = 30 \text{ per cent}$$

of hydrous mica. If the proportion of alkali in the hydrous mica is lower, the relative amount of this mineral in a clay will be higher still.

It is usually permissible to ascribe the *total* alkalies to the hydrous mica as the amount of exchangeable bases, soluble salts and other alkali-bearing minerals is generally insignificantly small.

Other minerals which may be present in fireclays include *ironstone*, *anatase* (TiO_2), *carbonaceous material* and *amorphous material*, consisting of silica and alumina which appear to be present as a cementing medium in the clay. Traces of the kaolin mineral *dickite* have also been found in some clays, possibly derived from the ironstone nodules which frequently contain the mineral encrusted around the central nucleus. Traces of many other minerals may be present and occasionally some fireclays contain a considerable proportion of an unusual mineral: these are exceptional, however, and the vast majority of fireclays conform to the general pattern.

As *livesite* and hydrous mica in fireclays have average alumina contents of 39 per cent and 31 per cent (average) respectively prior to ignition, it is reasonable to assume that fireclays rich in silica contain appreciable quantities of free silica, whilst a high alumina content indicates a predominance of *livesite* or hydrous mica. Some differentiation between these two may be found from the alkali figure which will be comparatively large (above 2 per cent) if there is excess of hydrous mica.

A typical mineral balance sheet is shown in Table VI.V, for a fireclay from the Yorkshire area.

The constitution of the colloidal amorphous material has been deduced by difference from the chemical balance, although its amount is in accordance with that given by thermal analysis.

The mineral compositions of typical fireclays from some other localities are shown in Table VI.VI.

TABLE VI—V. COMPARISON OF CHEMICAL COMPOSITION AND MINERALOGICAL ANALYSIS OF A FIRECLAY

<i>Mineral</i>	<i>Per cent</i>	<i>SiO₂</i>	<i>Al₂O₃</i>	<i>TiO₂</i>	<i>Fe₂O₃</i>	<i>MgO</i>	<i>CaO</i>	<i>K₂O</i>	<i>Na₂O</i>	<i>Wt. +120°</i>	<i>Loss -120°</i>
Livesite	43.0	19.9	17.1							6.0	
Free silica	24.5	24.5									
Hydrous mica	22.0	10.5	7.0	0.2	0.7	0.1	0.1	1.3	0.3	1.8	
Ironstone	1.0				1.0						
Anatase	1.1			1.1							
Amorphous material	5.0	1.7	2.8							0.5	
Organic matter	1.2									1.2	
Adsorbed water	1.3										1.3
Total	99.1	56.6	26.9	1.3	1.7	0.1	0.1	1.3	0.3	9.5	1.3
By chemical analysis	99.3	56.6	26.9	1.3	1.7	0.3	0.2	1.26	0.22	9.5	1.3

TABLE VI—VI. MINERALOGICAL COMPOSITION OF SOME FIRECLAYS

	<i>Scottish</i>		<i>Yorkshire</i>		<i>Stourbridge</i>
	1	2	1	2	
Livesite	68.0	62.3	43.5	39.1	42.4
Free silica	1.2	0.3	24.8	12.3	7.1
Hydrous mica	23.4	16.6	22.6	43.0	46.3
Ironstone	2.2	1.6	1.0	0.8	1.0
Anatase	1.6	1.5	1.1	1.6	1.0
Carbonaceous material	1.0	12.3	1.2	0.3	0.2
Colloidal matter	2.2	4.9	4.9	1.6	1.1
Total	99.6	99.5	99.1	98.7	99.1

The *size distribution* of minerals in fireclays can be deduced by analysing the mineralogical composition of each sedimented fraction. The grain size range of the principal minerals in a clay is at least as important as the total mineralogical constitution in influencing the properties of that clay. This is demonstrated in other sections where actual grain size distributions are quoted. The hydrous mica may be present either as comparatively coarse grains (above 30 μ) or it may be in the form of particles as small as the kaolin clay mineral itself. At high temperatures the small-sized micaceous flakes react more rapidly than large ones and therefore the behaviour of the clay can be predicted only from a knowledge of the amount *and* grain size distribution of each mineral.

Super-duty Fireclays and High Alumina Clays. In recent years the need has arisen for fireclay refractory bricks capable of withstanding temperatures higher than those formerly used. Manufacturers in the United States have developed *super-duty fireclay bricks* to meet this need and although supplies of high alumina clays are not

common in this country, the development of a similar product is progressing favourably.

The range of composition in high alumina fired bricks is:

Silica	45-55 (average 51.5) per cent
Alumina	39-48 (average 42.5) per cent
Iron oxide	less than 2 (average 1.0) per cent
Titania	about 2 (average 2.1) per cent
Lime	less than 0.5 (average 0.3) per cent
Magnesia	less than 0.5 (average 0.2) per cent
Potash, Soda	less than 1.5 (average 0.8) per cent

There are bricks of slightly inferior quality described as *high duty fireclay bricks* with an alumina content of about 3 per cent lower than the average shown above.

High quality fireclay bricks are manufactured from clays with a low free silica content and the chief components are essentially a kaolin mineral and hydrous mica. Some Scottish clays and some from Northumberland are of suitable composition, except for their iron content which is usually too high. This would not be too serious a limitation if the iron were disseminated uniformly throughout the clay, but in many cases it is present as nodular ironstone which gives rise to *black* or *brown* spots and localised *bloating* at high temperatures.

Excellent high alumina bricks are made from calcined china clay, commercially termed *molochite*, although they are rather expensive. Other high alumina bricks are manufactured from raw materials which are hydroxides of alumina mixed with a little clay.

For further information on refractory clays see A. B. Searle's *Refractory Materials: their Manufacture and Uses* (London, C. Griffin and Co. Ltd.).

Bonding Clays. Some clays are of value as bonding agents. They are used for increasing the strength of moulding sands employed in the metal-casting industries. In order not to reduce the desirable properties of the sand, only small quantities of clay may be added, therefore, it must be of high binding power. Montmorillonite-type clays are frequently employed, but plastic kaolin clays are sometimes preferred. This latter clay is not of common occurrence, but a few have been developed commercially in the British Isles.

Such bonding clays are soft-textured and have been formed under geological conditions where the separation of most of the undesirable minerals has been achieved and only fine-grained components are present. The two principal minerals are *livesite* and *hydrous micas*, but the grain size of these is very much finer than in fireclays.

Bonding clays of high plasticity are sometimes added to non-plastic material in the manufacture of high refractory bricks, e.g. aluminous bricks.

Building Brick Clays¹ depend for their value on their physical properties rather than their chemical composition and, consequently, the permissible range of composition of a brick clay is very wide. The principal properties required in a clay for brickmaking purposes are that (a) it shall be present as a deposit sufficiently extensive

¹ Many brick clays are also suitable for making roofing tiles, terra-cotta and coarse earthenware ('brownware').

and accessible to warrant large-scale development,¹ (b) it shall be plastic enough to mould easily into shape and retain that shape in both wet and dry states, and (c) it shall vitrify sufficiently at a temperature of 950–1100° C. to form hard bricks without excessive shrinkage or deformation.

The clays which satisfy these requirements *perfectly* are limited, and although there are many which can be used quite satisfactorily, it is wrong to assume that any deposit of clay can be used for making building bricks.

The clays used may contain from 35–90 per cent of silica, the average being about 65 per cent. It is better to have a high silica content for this indicates the presence of considerable proportions of sand, which reduces the overall shrinkage of the clay on drying and firing, and provided the strength in the wet and dry states is not too low as a consequence, the more sand present the better will be the fired shape. If the clay mineral present is exceptionally plastic, a clay with large amounts of free silica (sand) can be used with advantage.

Brick clays (with the exception of those used for firebricks) may usually contain a comparatively large proportion of metallic oxides (fluxes), as such clays are not heated to a sufficiently high temperature to cause distortion due to excessive fusion. In the absence of a moderate proportion of these oxides, the brick will be deficient in vitrifiable bonding material, and so will be relatively weak. With a suitable amount of fluxes, bricks of enormous strength can be produced, each particle of unfused material being held in place by the crude glass formed when the fluxes combine with the silica in the clay. Clays suitable for building bricks may contain up to 15 per cent of alkalis (the average being about 8 per cent), up to 15 per cent of calcium compounds expressed as lime (the average being below 2 per cent), and up to 7 per cent of magnesia (the average being about 1 per cent). Iron compounds (expressed as ferric oxide) occur in proportions up to 32 per cent, the average being 3–8 per cent; the red colour of many bricks is due to the fully-oxidised iron compounds present and the colour of 'blue' bricks to the reduced iron compounds present. Some analyses of brick clays will be found in A. B. Searle's *Modern Brickmaking*.

Some clays which shrink excessively, and others which have a poor colour when burned, are improved by the addition of sand, especially if this contains a considerable proportion of iron compounds other than pyrites.

The metallic compounds most likely to cause trouble in the manufacture of building bricks are (a) limestones, and (b) soluble salts. The limestones produce lime which slakes in moist air and may crack the bricks. This may be largely avoided by grinding the limestones to a fine powder, as particles less than 0.04 in. in diameter seldom crack bricks containing them, even when present in amounts up to 15 per cent.

Calcium compounds confer certain advantages on a clay for building brick purposes provided that they are finely divided. They are of value in some clays rich in iron, for they produce a pleasing buff or fawn colour on firing, and prevent the formation of a 'red brick'. Calcium compounds are also of value as a binder or glass-

¹ For an output of ten million bricks per annum for twenty years there must be at least 800,000 cu. yds. of suitable *excavatable* material; this, at an average thickness of 3 yds., would occupy 55 acres of land (i.e. 266,200 sq. yds.), apart from that needed for margins and for the works.

A clay seam 3 feet in thickness will yield about 5,000 tons of clay per acre.

producer on firing, but in excess they tend to cause premature fusion and distortion of the bricks.

Soluble salts are chiefly objectionable because they form a white efflorescence or 'scum'; consequently, brick clays containing an appreciable proportion of soluble salts can be used only where the appearance of the fired bricks is of no importance.

Building-brick clays are of many types and the principal ones,¹ classified on the basis of their geological age, are:

1. *Carboniferous* or *Coal Measure* clays, which are of poorer quality than would be used for refractories. Bricks from such clays are manufactured in many parts of the country. The Etruria marl clays are of this classification. In 1938, about 33 per cent of all building bricks produced were from Carboniferous clays.

2. *Triassic* clays outcrop extensively along a band between 3–20 miles wide from the mouth of the Tees through the Midlands, Gloucestershire, Somerset and Devon. Another outcrop can be traced from the coast of Lancashire to its mergence with the former in Staffordshire and in this region the deposit is extensive. The most valuable clay is the Keuper Marl.

3. *Jurassic* clays—chiefly of marine origin—which include the well-known Oxford and Kimmeridge clays, so highly prized by brickmakers. These clays outcrop along the length of the British Isles from Yorkshire to Dorset, but it is in the Peterborough and Bedford areas where the deposit is most extensively worked. Bricks made from Jurassic clays make up more than one-third of the total production in this country.

4. *Cretaceous* clays are worked in the South-east of England, the principal being the Hastings, Weald and Gault beds. Although the total production of bricks from clays of these beds is comparatively small, the quality and colour of the ware is excellent.

5. *Tertiary* clays include those of the Reading beds and the London clay.

6. *Recent* clays are found in the valleys and flood-plains of large rivers and are termed alluvium or brickcarths. The important ones for brickmaking are argillaceous soils and although such deposits are not extensive, they are comparatively easy and cheap to work.

7. *Glacial* clays are the detritus left by the receding ice-pack following the Ice Ages. They may be in the form of moraines, but much more commonly as Boulder Clay, so called because of the large rock fragments which are always present. Many deposits are of good commercial value, but the clay is extremely variable in composition and properties.

The geological formation of British building-brick clays has been described by Keeling.²

There is little published data on the constitution of building brick clays, but it is certain that they are generally more complex than the clays previously considered.

It may be inferred that the *Coal Measure* clays will be similar to fireclays, but with a higher proportion of silica and alkali impurity. Many surface outcrops are worked and it is customary to extract the softer clays by quarrying. Consequently,

¹ Bonnell, D. G. R. and Butterworth, B., *Clay Building Bricks of the United Kingdom* (H.M.S.O., London, 1950).

² Keeling, P. S., *Trans. Brit. Ceram. Soc.*, 52, 465, 1953.

more than one clay seam is often excavated along with intervening strata of grits, shales and sometimes coal.

The geology of the *Jurassic* clays has been worked out in detail, but the complete mineralogical analyses are not known with certainty. The clays are of marine origin, so that shells and other fossils are of common occurrence. Carbonaceous material is also present, sometimes in considerable quantity, and is of value in the burning of the clay. Unlike Coal Measure clays which frequently contain coal, the *Oxford clay* is rich in algae or oil shale which burns readily at comparatively low temperatures. It is likely that the principal mineral in the clay is of the kaolin-type, but there is an associated alkali-bearing mineral which may be glauconite. Quantities of sand are also present. Oxford bed clay is of value because the associated carbonaceous material reduces the fuel required in the firing, and the high lime content, derived from the marine fossils, produces a pleasing colour, although it tends to shorten the vitrification range of the clay.

Clay of the later geological periods has an extremely complex mineralogical composition. Honeyborne¹ has reported that clays from the *Hastings bed*, which outcrops in Kent and Sussex, contain kaolinite which is not well-crystalline (live-site?). Hydrous mica (illite) and a chloritic mineral along with iron hydroxide as lepidocrocite, hæmatite and considerable free silica sand are also present. Some samples also contain calcite and small proportions of gypsum. The same author² has also described clays from the *Keuper Marl* which is another important and extensive building brick clay deposit. The principal mineral component is of the hydrous mica or illitic type and, in addition, a complex mixed-layer mineral of chloritic and montmorillonite-type is present. Additional minerals include calcium carbonate (in the form of fossil remains), hydrated iron oxide, free silica sand and magnesium carbonate.

Alluvium or *recent* clays have not been examined in detail largely because they occur as isolated pockets which are unrelated to other parts of the same area. Samples from small workings in the flood plain of the Humber contain hydrous mica, sand and hydrated iron oxide (goethite), along with a kaolin-type mineral.

Glacial drift is also used for making building bricks and few analyses of this material have been made. The minerals present in them are derived from the areas which were covered by the ice sheet. The impurities or non-clay minerals are usually greater in amount and of larger grain size than those in a water-sedimented clay.

Engineering brick clays are of similar type to those used in making building bricks. A larger proportion of fluxing agents is desirable so as to produce a stronger, harder, more vitrified and impervious body than that of other bricks.

Clays for Ceramic Ware.³ The clays used in the manufacture of different wares are selected chiefly on the basis of physical properties, though the importance of chemical composition must not be ignored. *White ware* of all types—including porcelain, bone china, fine earthenware and vitreous table ware is made from white-

¹ Butterworth, B. and Honeyborne, D. B., *Trans. Brit. Ceram. Soc.*, 51, 211, 1952.

² Honeyborne, D. B., *Clay Min. Bull.*, 1, 150, 1951.

³ The term *pot clay* or *pottery clay* has so wide an application as to be almost useless. It is applied to the refractory clays used for crucibles employed for melting steel and other alloys and the 'covered pots' used in glass manufacture and to the clays used for coarse and fine earthenware and for the various kinds of porcelain.

burning clays, principally kaolinite, with additions of ball clay to promote strength in the moulded shapes. *Permeable hollow-ware*, which includes heavy clays, refractories, terra-cotta, coarse earthenware, faience, majolica and many others is made from clay which does not vitrify excessively at the temperature of firing. Colour is usually of secondary consideration in these bodies, so that many types of clay can be employed. *Impermeable ware*, includes vitreous china, porcelain and stoneware which have dense non-porous bodies; the two former are white or light cream coloured, but stoneware varies from almost white to buff or dark brown. Clays with a high proportion of fluxing elements are required for the manufacture of stoneware, and it is common practice to add extra ones during manufacture. The clay should be fine-grained and free from large particles of sand or mica. The composition of ceramic bodies is discussed more fully on pp. 333 ff.

Montmorillonite-type Clays. Clays consisting largely of montmorillonite minerals are not common in the British Isles, but are of frequent occurrence in many other parts of the world.

Experimental work on the synthesis of clay minerals by Noll¹ and by Strese and Hofmann² has suggested that the formation of these minerals is favoured by alkaline conditions. Ross and Hendricks³ have concluded that orthoclase feldspar and muscovite will not weather to montmorillonite unless there is a sufficient supply of magnesium, ferric or ferrous ions available in an alkaline medium. Some 'fuller's earths' which contain montmorillonite, appear to have been derived from plagioclase feldspar, but the most frequent mode of formation is direct surface weathering of volcanic glasses, especially when these are rich in magnesium or iron.

Sedimentary deposits of montmorillonite minerals and the associated impurities are formed by the leaching of altered rocks and the deposition of transported material at some point removed from the original source. These impure montmorillonite-type clays are often termed *bentonites* and are of frequent occurrence in the Cretaceous beds of Wyoming, U.S.A., in Alberta, Canada and many other localities.

Clays containing montmorillonites are valued for their *binding power* and the strength which they impart to other materials. Some samples have a high adsorptive capacity and are useful in purifying or bleaching oils, and in the paint industry where they are called *fullers' earths*.

Fullers' earth is mined in two localities in England, although similar clays may occur in other places. The principal deposits are near Nutfield in Surrey and Bath in Somerset. The origin of the British fuller's earths is still unknown; they present the anomaly of an apparently altered volcanic ash occurring in the middle of arenaceous beds of sedimentary formation. It has been suggested by Newton⁴ that the clay has its origin in chemical precipitation in marine waters where normal sedimentation was almost non-existent. Apparently at some stage in the formation of the Lower Greensand deposits, land movements occurred which produced sheltered marine conditions for a comparatively short duration. Newton's theory is the most likely, for no volcanic material was associated with the geological periods in question.

¹ Noll, W., *Neues. Jahr. Chem. der Erde.*, 10, 129, 1936.

² Strese, H. and Hofmann, U., *Zeit. anorg. All. Chemie.*, 247, 65, 1941.

³ Ross, C. S. and Hendricks, S. B., *U.S. Geol. Survey Prof. Paper* 205-B, 1945.

⁴ Newton, E. F., *Geol. Assoc. Proc.*, 48, 175, 1937.

Chemical analyses of samples of Wyoming bentonite and Nutfield fullers' earth are given in Table VI.VII.

TABLE VI—VII. CHEMICAL ANALYSIS OF
MONTMORILLONITE CLAYS

	Wyoming bentonite	Nutfield fullers' earth
	per cent	per cent
SiO ₂	49.40	54.36
Al ₂ O ₃	20.40	12.22
TiO ₂	0.40	0.72
Fe ₂ O ₃	3.70	2.91
FeO	n.d.	3.02
MgO	2.55	2.32
CaO	1.80	2.48
Na ₂ O	0.43	0.21
K ₂ O	1.12	0.61
H ₂ O (moisture)	5.00	5.60
H ₂ O (lost at 900° C.)	15.15	15.91
Total	99.95	100.36

The mineralogical composition has not been deduced in detail. The main mineral in both samples is montmorillonite (see p. 148). Kerr, Main and Hamilton¹ state that the impurity content in the Wyoming sample is about 10 per cent, principally quartz and feldspar with some calcite, limonite and glauconite. The Nutfield sample is similar but also contains traces of pyrites and sphene.

The nature of the principal minerals in a clay deposit can, to some extent, be predicted from the geological details of the deposit. Hydrothermal alteration of an igneous rock will usually produce a kaolin mineral and hydrous micas if acid conditions are prevalent, but montmorillonites if the attack is under alkaline conditions. Surface weathering also favours the formation of kaolin minerals unless excess magnesium or iron in an alkaline medium is readily available. Hydrous micas or illites are of common occurrence particularly in marine-deposited shales, and it is a remarkable fact that these minerals are frequently associated with the kaolin-mineral livesite in a way which suggests inter-convertibility between the two forms.

Many deposits of early geological periods contain only hydrous mica and a kaolin mineral, along with free silica and minor constituents. More recent formations may contain more complex forms such as *chlorites* and, in some cases, *vermiculites*. These latter minerals are known to be less stable than other clay minerals and they may, in the course of geological time, revert to the hydrous mica or kaolin types.

It is important to realise that when a bed of clay extends over a large area, it may vary considerably in properties in different localities. Thus, the Middle Lias clay of Oxfordshire is very different from clay from the same seam which outcrops in Dorset; similarly, a valuable bed of fireclay in one area may be worthless when it is found in other regions.

¹ Kerr, P. F., Main, M. S. and Hamilton, P. K., *Amer. Petroleum Inst. Res. Proj.* 49, Part 5 (Columbia Univ., N.Y., 1951).

Even when taken from two closely-separated areas, a particular clay may show considerable variation. The difference between a deep-mined clay and the same seam under shallow overburden is so well marked that it is often impossible to use the two materials for the same purpose. A striking change in the plastic behaviour of a clay often occurs when it is taken from land on which there has been intensive cultivation. The fertilisers used in the soil are sufficient to alter the exchangeable cations even in clays at a considerable depth and so change their character.

SILICA AND SILICEOUS MATERIALS

FREE silica is second only to clay as an important ceramic material. It is used on a large scale: (i) in the glass industry; (ii) for making bricks, roofing tiles, refractories and ceramic wares; and (iii) in the form of sand for a variety of industrial processes. As with clay, the forms in which free silica is present together with the nature of the impurities have a profound influence on the properties of the material both in its raw and fired states.

The principal siliceous materials (other than clays) which occur in nature and are used in the ceramic industry include (a) crystalline quartz, (b) silica rocks, including quartzites, sandstones, ganisters, silcrete, etc., (c) silica sands, and (d) amorphous or 'organic' silica including flint, diatomaceous earth, etc.

Free silica occurs in a variety of forms and makes up a large portion of the earth's crust, something like 60 per cent of which consists of this mineral, either in bulk or disseminated through other rocks in particles of varying sizes. Free silica is present in both crystalline and amorphous conditions, the principal forms being:

Amorphous silica occurs as (a) precipitated silica formed by the deposition of silica from solution; (b) siliceous skeletons of diatoms, etc., in such forms as kieselguhr, tripoli, etc.; and (c) silica glass, which is of infrequent occurrence in nature, but common in manufactured clay products and formed by rapid cooling of molten silica.

Precipitated silica occurs in various forms in nature, the commonest being flint, chert, chalcedony, opal and geyserite. *Flint* consists of silica which has been precipitated around a nucleus of either organic or inorganic matter and, consequently flints often contain a variable proportion (usually about 5 per cent) of impurities, chiefly of carbonaceous and calcareous matter. It occurs as grey or black nodules of varying size, of great hardness, which break with a conchoidal fracture. Sosman¹ considers that it consists of an intimate mixture of amorphous and crystalline silica. Flint is found usually in the form of pebbles, especially on the sea-shore, where they often extend over large areas. They also occur in beds of clay or chalk—especially those of Cretaceous age—one bed being known as *clay-with-flints*. Small grains of amorphous silica occur to a varying extent in clays, sands, and similar detrital deposits.

Chert or *hornstone* is similar to flint, being formed by the deposition of sponge spicules producing greyish, brown or black grains of almost crystalline appearance, though in reality it is truly amorphous. The grains occur in beds of limestone, clay,

¹ Sosman, R. B. *The Properties of Silica* (Chem. Catalog. Co., N.Y., 1922).

sand, and sand-rocks, especially those of the Carboniferous Age, in which they frequently form large masses of stone.

Chalcedony is a somewhat fibrous variety of precipitated silica formed in the same manner as flint and chert. Some specimens may have a deformed quartz network structure with considerable micropores running through them. Chalcedony varies in colour from white to blue or brown and has a hardness of 7 and a specific gravity of 2.55–2.58, a refractive index of about 1.54 (rather less than that of quartz), and a slightly lower birefringence than quartz. *Onyx*, *agate*, and various other minerals resemble chalcedony so closely that for the purpose of the present volume they need not be distinguished.

Opal is a hydrated form of silica with the composition $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ where the percentage of water is usually less than 10. It is found in rocks of many kinds, but is of secondary origin behaving as a dried-up gel filling cracks and fissures and cementing grains of other minerals. It commonly occurs in sandstones and shales, and is readily converted into chalcedony on heating. When in massive form, opal is highly prized as a gem-stone, but it is difficult to identify when disseminated throughout a rock mass. The specific gravity of opal is 2.2. It is isotropic between crossed nicols.

Diatomaceous earth or *kieselguhr* and *radiolarian earths* are mainly opaline silica and are of value as thermal insulators. Diatoms and radiolaria are minute organisms which have siliceous skeletons; they thrive in situations where there is abundant available silica in solution, as in the Miocene beds of California where volcanic emanations of a siliceous character have promoted growth. The remains of such organisms have accumulated as large deposits on sea- and lake-beds in some places. The intrinsic nature of the skeletons of silica results in the formation of a mass containing appreciable volumes of entrapped air, so that these earths form almost ideal thermal insulators, and in addition, are of value as an absorbent or filtering medium and as surface catalysers. The chief deposits are in the United States, Germany, Denmark and North Africa, but workable seams are found in the Isle of Skye, Cumberland and Northern Ireland.

The *impurities* in diatomaceous earths and similar materials are chiefly silt, clay, sand, volcanic ash and decayed organic matter. Many samples are red in colour indicating a high proportion of iron oxide, although some American deposits are almost white. Unfortunately, the refractoriness of diatomaceous earths is low and it is inadvisable to expose them to a temperature of greater than 900° C.

Geyserite is another form of opal and occurs as a loose, porous form of silica precipitated from solution around hot springs, as in Yellowstone Park, U.S.A., in Iceland and elsewhere.

Le Chatelierite is the only form of silica glass found in nature and is of very rare occurrence.

Colloidal silica may occur either (a) in bulk as a horny mass in forms such as those mentioned above; (b) as a cementing material in other rocks, such as quartzites, sandstones, etc.; or (c) as an active colloidal substance possessing highly absorbent properties.

Crystalline silica occurs in nature in three forms, the commonest being quartz, whilst tridymite and cristobalite are relatively rare. The two latter forms are

produced by heating silica to high temperatures, as in the manufacture of silica bricks and other siliceous articles.

Quartz occurs as hexagonal or rhombohedral crystals, which are colourless when pure, but are often stained a variety of colours on account of the impurities present. Whilst this form is typical of quartz, a closer examination will show the presence, on some crystals, of small triangular facets, which show that the symmetry of the quartz crystal is restricted to one vertical axis of threefold symmetry, because no centre of symmetry can exist in two enantiomorphous forms, one of which rotates a ray of polarised light to the left (i.e. it is laevo-rotatory) and the other to the right (i.e. dextro-rotatory).

Quartz has a conchoidal fracture, a hardness of 7 and a specific gravity of 2.65. Its refractive index is 1.55 and its birefringence 0.009. It is often readily recognised under the microscope by having numerous inclusions which cause it to be cloudy or opaque.

Quartz occurs also (i) in massive form, (ii) as small grains disseminated through other rocks, and (iii) as sand. The most useful forms of massive silica are (a) *quartzites*, which consist of an irregular mosaic of grains of quartz cemented by a siliceous cement, (b) *silica rocks*, which are grains of quartz united by a cement, preferably of a siliceous nature, but generally containing more impurity than quartzites, and (c) *ganisters*, which consist of small, highly angular grains of quartz.

Tridymite is not of common occurrence in nature, but it has been reported in rocks of recent volcanic formations, and it is a constituent of some rhyolites. It forms pseudo-hexagonal crystals with characteristic arrowhead twinning, with a specific gravity of 2.28 and a refractive index of 1.477. Tridymite is the stable silica modification between 870° C. and 1470° C.; it is therefore a common constituent of fired siliceous materials.

Cristobalite is another crystalline variety of silica which again is rarely found in nature. Occasionally cristobalite is present in volcanic rocks and is named after the locality San Cristobal, Mexico, where it is a constituent of andesite. It forms pseudo-cubic crystals with a specific gravity of 2.32 and a refractive index of 1.484. It is the crystalline form of silica which is stable at temperatures above 1470° C.

SILICA ROCK FORMATIONS

THE various silica rock formations which are of value in ceramics are composed of crystalline or amorphous varieties, or usually admixtures of the two types. They vary considerably in character and property.

Crystalline quartz is the essential raw material for the manufacture of silica glass, where the impurities must be at a minimum. The purest form of silica in nature is rock crystal or crystal quartz, which occurs in veins or geodes penetrating other rock formations. The crystals, which are often perfect in form and range in size from a few millimetres to several centimetres, are the result of the slow evaporation of solutions rich in silica, or of the slow cooling of siliceous magmas. In only a few localities do such crystals occur in quantity, the main sources of supply for British industries being Madagascar and Brazil. Crystal quartz which can be washed free from any adherent associated impurity provides a material which is at least 99.98

per cent silica on analysis. Occasionally liquid or gaseous inclusions within the crystals are present, and also other minerals such as rutile (TiO_2), tourmaline, tremolite or chlorite, which cannot be removed without destroying the crystal.

Pure quartz melts at 1690°C. to form a highly viscous transparent liquid which can be supercooled to a glass without forming any crystals.

Silica sands are used in the manufacture of glasses of all descriptions; a material of high purity is required. Some sands, of which that from Loch Aline is an example, are pure enough to be used in the manufacture of silica glass.

The role of silica in glasses is that of an acid medium to combine with the alkaline constituents, and it is important to employ sands of great purity. The particles of sand must be small so as to ensure rapidity of reaction. Best quality glass sands contain more than 99.5 per cent of silica, but commoner ware, such as some bottle-glass can be manufactured from material with as little as 65 per cent of total silica.

The principal *impurities* which occur in glass sands are:

(a) Alumina, in the form of felspar, muscovite or clay; the two latter minerals can be removed fairly easily by washing. In most glasses a small proportion of alumina is not serious and for some purposes alumina is added to the batch to impart tenacity to the glass ware.

(b) Iron compounds, which may be present as a film coating quartz particles, or as discrete particles of haematite, magnetite or ilmenite. Iron is most undesirable as an impurity, as it has a profound influence on the colour of the glass as shown in Table VI.VIII.

TABLE VI—VIII. EFFECT OF IRON OXIDE
ON THE COLOUR OF GLASS

<i>Colour of glass</i>	<i>Ferric oxide added</i>
Colourless	Less than 0.02 per cent
Nearly colourless	0.02–0.05 " "
Faintly green	0.05–0.10 " "
Yellowish green	0.1–0.3 " "
Green	0.3–1.0 " "
Dark green	1.0–2.0 " "

These figures are only approximate indications of the relation of colour to iron content. The effect can be mitigated, to some extent, by the addition of a decoloriser such as manganese dioxide, nickel oxide or selenium.

(c) Lime and alkalis, mainly in the form of felspar or micas, are not serious as impurities, as large amounts of these constituents are purposely added in the production of commercial glasses.

Many sands of good quality are found in the British Isles although most have to be pre-treated in some way before they can be used for making glass.

Raw Materials for Silica Refractories. Silica bricks¹ are usually made from

¹ Sand-lime bricks are made chiefly of silica (sand) but the term *silica bricks* is commercially restricted to highly refractory bricks made from selected silica rocks. Sand-lime bricks are not refractory.

rock containing at least 97 per cent of silica, but the following range of compositions is usually permissible:

Silica	95-99 per cent
Alumina	0.1-2.8 per cent
Iron oxide	0.3-1.3 per cent
Lime	0.2-2.4 per cent
Soda and Potash	0.2-1.5 per cent

The raw materials used are mainly sedimentary sand deposits which have been cemented with precipitated silica and have formed a hard, dense rock mass.

The conversion of the siliceous raw material to cristobalite or tridymite must be completed in a reasonable time at temperatures of about 1450° C. For this reason, pure quartz crystal would not be suitable because its reaction is extremely slow even in the presence of catalysts. Amorphous silica, on the other hand, converts too rapidly, sometimes with disastrous effects on the brick shape. The ideal raw material is one composed of small grains of quartz which contains a proportion of a non-crystalline, flint or chalcedonic type of silica, which will be readily converted and 'seed' the slower reacting crystalline material.

Lower grade silica bricks are made from sandstones and ganisters with a total silica content between 87-96 per cent. The impurities are mainly mica or hydrous mica, limonite and occasionally a kaolin-type clay mineral. The first silica bricks were made in the early 1820's from Dinas rock found in South Wales, and although this material is no longer used for high quality bricks, similar material is in frequent use on the Continent at the present time for what are described as *Dinas bricks*.

For many purposes, various silica rocks, which form part of the Millstone Grits, have been used for many years and are still in use although on a much smaller scale.¹ With the ever-increasing demands of metallurgists for furnace linings which will withstand greater temperatures, some of these silica rocks are unsatisfactory because they contain small amounts of impurity, particularly alumina, which reduces very seriously the refractory properties of the bricks. It is also advantageous to use material with a low porosity and one in which the individual crystallites of quartz are as small as possible.

The principal sources of high-grade silica have been summarised by Davies² as follows:

1. *Coarse-grained quartzites* including the Welsh quartzite mined in the region of Bwlchgwyn, and incoherent pebble deposits, as near Aberdeen, both of which are mainly composed of comparatively large fragments of quartz grains which have been cemented by secondary precipitated silica. The Welsh rock is contaminated with hydrous mica (*sericite*), which is the main source of alumina. Davies has stated that the cementing silica crystallises as quartz which develops on the surface of the original particles, thereby producing a mass of interlocked crystals. Grimshaw, Westerman and Roberts,³ however, have pointed out that Welsh quartzites rarely

¹ For a description of the historical development of silica bricks see Lynam, T. R., *Ceramics, a Symposium* (The British Ceramic Society, Stoke-on-Trent, 1953), pp. 448-73.

² Davies, W., *Trans. Brit. Ceram. Soc.*, 51, 95, 1952.

³ Grimshaw, R. W., Westerman, A. and Roberts, A. L., *Trans. Brit. Ceram. Soc.*, 47, 269, 1948.

Other Sands. Many other sands are used in ceramic practice, and their value in a particular application depends on their physical and chemical properties. Sands for brick-making purposes must be relatively cheap and if they are required in large quantities they must occur near the site on which the bricks are manufactured. Some clays from the London Basin shrink excessively on drying and firing, but, because they are highly plastic, a proportion of sand from nearby deposits can be incorporated to improve their quality.

A special quality of sand is required in the manufacture of *sand-lime* bricks. Five per cent of lime is added to a sand which contains a proportion of fine particles. The moulded shapes are treated under steam pressure in an autoclave, so that reaction occurs between the lime and silica forming cementing substances. About 12–15 per cent of the sand should pass a 100-mesh sieve, and a third of this quantity should pass a 200-mesh sieve. The rest of the sand should be coarse with a centre grain size of about 30 B.S.S. Quite often two sands are blended to give the required particle size distribution.

Specifications for sands used for other purposes are given in *Sands and Crushed Rocks* by A. B. Searle (see p. 316).

ALUMINA

ALUMINA occurs in a variety of forms. It is a common constituent of many rocks and minerals, but it is also found in the free state as the oxide or hydroxide.

Alumina is present in nature in massive form and as grains disseminated through other materials principally as *corundum* (α - Al_2O_3), which occurs as grey, green, reddish or yellow hexagonal crystals, having a hardness of 9 and a specific gravity of 3.9–4.1. Corundum is mined only on a small scale because all the known deposits are limited in extent. The principal sources are Asia Minor, South Africa, Greece, Canada and the United States.

Artificial corundum is prepared by fusing bauxite, and is being increasingly used as a refractory material on account of its high softening point, inertness to corrosion and constancy in volume when heated.

Alumina is more prevalent in the hydrous form as *bauxite* and *laterite*, which are apparently amorphous, granular materials of a white or brownish colour according to the amount of iron oxide they contain; the main minerals in these types of deposits are: (a) *diaspore*, $\text{AlO} \cdot \text{OH}$ or $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, which consists of white orthorhombic crystals, with a hardness of about 7 and a specific gravity of 3.5; and (b) *gibbsite*, $\text{Al}(\text{OH})_3$ or $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, which usually occurs in concretionary masses and rarely as monoclinic crystals. It has a hardness of 2.5–3.5 and a specific gravity of 2.3–2.4.

Bauxite is not a simple mineral, but a term used to describe a massive formation which is rich in alumina. Most bauxites are mixtures of the mono- and tri-hydrates of alumina with some clay, but some samples which are loosely termed bauxite are almost entirely kaolinite. Bauxitic deposits are fairly widespread; some have been derived from basaltic rocks and others from rhyolites. Extensive valuable areas occur in British and Dutch Guiana, Australia, Yugoslavia, France, Hungary, the United States, Russia and elsewhere.

Smaller (commercial) quantities occur in Co. Antrim, Northern Ireland and the high-alumina fireclays of Ayrshire appear to be of similar origin.

Laterites are usually formed by the chemical alteration of certain igneous rocks, such as basalt lavas and rhyolites. They sometimes occur as primary deposits but much more commonly as a secondary formation. They consist chiefly of *gibbsite*, with some *boehmite*, *kaolinite* and occasionally some *chamosite*. The composition of laterites is very varied; they show every gradation from a highly ferruginous hydroxide with little alumina to almost pure aluminium hydroxide.

Lenses of lateritic material occur in some American fireclays and thus give a clay with a high alumina content, although of somewhat variable composition.

High alumina bricks are manufactured from natural bauxites which contain between 60 and 90 per cent alumina on a calcined basis. The main impurity is clay, usually of a kaolin type, which serves as a binder. Variable amounts of iron (0.5–12 per cent) and free silica (3–25 per cent) may also be present. Materials which are rich in diasporé are generally preferred to those containing gibbsite, because the lower content of water of constitution in the former results in considerably less shrinkage on firing. This can be mitigated by pre-calcining the gibbsite.

Aluminous refractories cover bricks ranging from about 44–99 per cent Al_2O_3 . Because natural aluminous clays are uncommon in this country, the range of refractories of this type which are produced is limited. Synthetic mixtures of impure bauxites and clays are being used on an ever-increasing scale to produce good quality bricks. Commercial refractories corresponding to the ideal composition of *mullite* (i.e. *circa* 72 per cent) and others with about 90 per cent alumina are manufactured on a large scale. Aluminous clays are quite common in the United States and a wide range of refractories is made from them.

Alumina materials of great purity have been developed for many purposes. The raw material is bauxite and the alumina is extracted in acid solution in an autoclave, then reprecipitated and the final traces of impurity are removed by leaching. The product, which contains upwards of 99.5 per cent alumina is shaped and fired at 1750–1800° C. It is termed *sintered* or *fused* alumina and it has virtually zero porosity. The high cost of processing restricts the use of such material to small scale specialised articles, although a refractory material containing 96 per cent of alumina is being used commercially for making standard-sized bricks.

High-grade fired alumina is also used in abrasive wheels, laboratory ware, cutting tools, turbine blades, sparking plugs and for making guides which form the threads of synthetic fibres. Alumina powder has largely replaced silica sand as a setting material for china biscuit.

ALUMINO-SILICATES OTHER THAN CLAYS

AN important group of high alumina refractories is made from the three aluminosilicate minerals, *kyanite*, *andalusite* and *sillimanite*, all of which have the composition $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, and on calcination at about 1650° C. are converted to *mullite*, $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$.

Kyanite occurs the most frequently; large deposits, usually in massive rock form, metamorphosed by heat and pressure, are found in Kenya, South Africa,

Australia, India and the United States. Pure crystals of up to 3 in. in length may be present in an interlocking aggregate contaminated with small amounts of pyrophyllite and quartz. Kyanite is also present in schistose materials, where kaolinite has been hydrothermally altered. On calcination to produce a stabilised form, kyanite undergoes a volume expansion of about 20 per cent.

Andalusite is less common, but deposits are worked for refractory purposes in Spain, South Africa and California. The principal form is a massive, metamorphosed rock, but fairly pure samples are occasionally found which have been weathered from such rocks and deposited elsewhere as silt or sand. The volume expansion on calcination is only about 4 per cent.

Sillimanite is becoming increasingly important and large deposits are being developed in Assam and India. Unlike kyanite, sillimanite undergoes scarcely any change in volume¹ (see p. 728), and the raw material can be used directly in furnace settings without any pre-firing. Sillimanite results from the metamorphism of pure clays; the Assam deposits are particularly pure, containing only minor amounts of quartz, biotite and cordierite, although there may be small amounts of excess alumina as corundum (α - Al_2O_3). The chemical composition of typical samples of the three minerals is shown in Table VI.X, along with some characteristic properties.

TABLE VI—X. COMPOSITION AND PROPERTIES OF
SOME ALUMINO-SILICATES

	<i>Kyanite</i> (<i>S. Africa</i>)	<i>Andalusite</i> (<i>California</i>)	<i>Sillimanite</i> (<i>Assam</i>)
	per cent	per cent	per cent
SiO_2	35.5	33.9	35.7
Al_2O_3	61.2	57.6	62.3
Fe_2O_3	0.9	1.6	1.7
TiO_2	1.1	1.5	0.2
CaO	0.1	1.3	Trace
MgO	0.2	0.8	0.1
Na_2O	0.1	—	{ Trace
K_2O	0.1	{ 0.6	
Loss on ignition	1.2	3.5	0.7
Refractive Indices	1.713–1.728	1.623–1.645	1.657–1.684
Specific Gravity	3.6	3.1–3.2	3.08
Hardness	7.5	7.5	7.5

Topaz, $\text{Al}_2\text{SiO}_4(\text{F}, \text{OH})_2$, is converted into mullite when heated to 1300°C . and so can be used in the manufacture of high-alumina refractories. The chief sources are Southern Rhodesia, Brazil and South Carolina, U.S.A.

Pyrophyllite, $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$, is an important raw material used for electro-ceramic bodies and in the manufacture of tiles. It is not of frequent occurrence in Britain, but in recent years workable deposits have been found in the Transvaal and Australia to supplement those of Carolina, U.S.A. The mineral is thought to have been formed by the hydrothermal replacement of acidic volcanic glasses. It occurs

¹ Griffith, C. F., *J. Soc. Glass Tech.*, 37, 222, 1953.

in massive flake-like form, not unlike mica, but softer and more brittle; although in colour it is silver-grey, it is often tinged with green as a result of chlorite inclusions. Other common impurities include quartz and hydrous mica, but many more are present as minor constituents. Pyrophyllite is valued for its low shrinkage on firing—it loses its water of constitution at about 600° C. and forms mullite and cristobalite above 1100° C. An analysis of a typical sample from North Carolina shows SiO₂ 77.4 per cent; Al₂O₃ 16.5 per cent; Fe₂O₃ 0.5 per cent; MgO 0.05 per cent; CaO 0.41 per cent; Na₂O 0.22 per cent; K₂O 1.26 per cent; and loss on ignition 2.87 per cent.

Alunite, K₂O.3Al₂O₃.4SO₃.6H₂O, is used to a small extent for the manufacture of tiles and other ceramic materials. It decomposes at a moderately high temperature to give a product rich in alumina (85 per cent) but with the remainder being virtually all alkali oxide—the shrinkage on firing is very large. It is formed as an alteration product of igneous rocks which are rich in alkalies and it occurs as seams or pockets. The principal deposits are in the Rocky Mountains of the U.S.A., Egypt and Australia.

FELSPARS, MICAS, PEGMATITES AND CORNISH STONE

FELSPARS and micas are minerals which are commonly used in the manufacture of glazes and in the preparation of vitrified bodies. Pegmatites and Cornish Stone are natural rock formations which are rich in feldspars and micas and are frequently used in place of the pure minerals.

Feldspar is a constituent of pegmatites, such as granite and other igneous rocks which are predominantly alkali-bearing; it may be present in amounts up to 60 per cent. Feldspar is also found in a reasonably pure state in Norway, Sweden, Russia and the United States, and it is readily purified from many rocks which contain it.

Feldspars are the most valuable fluxes used in the ceramic industries, both in 'bodies' and 'glazes', particularly in the manufacture of fine earthenware, china ware, porcelain and stoneware. Orthoclase and albite are preferred, but anorthite is sometimes used; for many purposes, feldspars can be replaced by the cheaper china stone.

None of the commercial feldspars is quite pure and their selection requires great care. One essential is that the feldspar should melt at a temperature not exceeding 1260° C. to form a smooth, glossy, vitreous mass, free from any discolorations, such as iron.

Mica is also present in igneous rocks and occurs in massive form in some localities. Muscovite mica is a valuable by-product in the production of china clay, because it is largely unaltered by the hydrothermal processes which formed kaolinite; the comparatively large plate-like grains of mica along with quartz particles are easily sedimented from the finely-divided clay mineral. The separation of the quartz is effected by sieving and screening. Mica is a valuable raw material for the electrical industry.

Both feldspar and mica are rich in alkalies, as shown by the theoretical analyses for the potassium-bearing minerals (Table VI.XI).

Nepheline or **nepheline syenite** is a rock which contains mainly nephelinite

$(\text{Na},\text{K})_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ and is used in place of felspar in pottery bodies and as a fluxing mineral in glasses. There are no workable deposits in this country, but supplies are imported from the United States where it is extensively employed.

Pegmatites are coarsely-crystalline rocks containing principally felspar, mica and quartz. The common form is granite, but the proportions of the minerals present in pegmatites are very variable.

TABLE VI—XI. COMPOSITION OF FELSPAR AND MICA

	<i>Orthoclase felspar</i> ($\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$)	<i>Muscovite mica</i> ($\text{K}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$)
	per cent	per cent
Silica	64.8	45.3
Alumina	18.3	38.4
Potash	16.9	11.8
Ignition loss	0.0	4.5

They are usually very hard rocks, having crystallised from a molten magma. They are mined in some localities, crushed and used as a foundation in making roads and for other purposes where a hard, durable material is required.

China stone may be described as a partially decomposed granite which, had the reaction proceeded further, would have produced a mixture of china clay, mica and quartz, with a little felspar. The best known samples in England are found in Cornwall and bear the names of *China stone*, *Cornish stone*, *moor stone* and *growan*. It contains china clay, felspar, quartz and unaltered granite in variable proportions, together with accessory minerals such as tourmaline, mica, topaz, beryl, zircon and fluor spar; the last-named is the source of colour of *purple stone*. It is not a definite mineral, but a heterogeneous mixture of the minerals just mentioned. The best qualities consist of felspar crystals in a quartz matrix, roughly in equal proportions, with a total alkali-content of about 7 per cent though the proportions of the various minerals vary greatly in the different grades.

Cornish stone in Cornwall is quarried, broken into lumps of convenient sizes and is then sorted into four principal grades:

(i) *Hard purple* which is the most fusible, contains the most felspar and is regarded as the most valuable grade.

(ii) *Mild purple* which contains less felspar and more china clay, and has a higher melting point.

(iii) *Dry white* contains still less felspar and more china clay and has the highest melting point. It is much softer than (i) and (ii).

(iv) *Buff stone* is slightly yellowish (due to iron compounds) and is unsuitable for white wares but satisfactory for some coloured ones.

The principal difference between the first three grades is in the degree of alteration. The kaolinite content is increased at the expense of the felspar, and there is a progressive increase in the content of secondary micas.

Typical analyses of the four grades as supplied by the manufacturers are in Table VI.XII.

TABLE VI—XII. CHEMICAL ANALYSES OF CORNISH STONES

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	Ignition Loss
Hard purple	71.7	15.6	0.2	0.1	2.0	0.1	4.0	4.7	1.4
Mild purple	72.4	15.8	0.2	0.1	1.8	0.2	3.5	4.0	1.9
Dry white	73.2	16.9	0.1	0.1	1.1	0.1	2.0	3.8	2.7
Buff stone	71.9	16.5	0.5	0.2	0.9	0.2	2.2	3.8	3.8

The changes in mineralogical composition in the samples can be followed by thermal analysis. The kaolinite and hydrous micas give characteristic thermal peaks. The approximate 'rational' mineralogical analysis of the above samples is shown in Table VI.XIII. A more accurate method of measuring the mineral composition of Cornish stone has been described by Keeling¹ using staining and point-counter techniques of microscopy.

TABLE VI—XIII. APPROXIMATE MINERALOGICAL COMPOSITIONS OF CHINA STONES

	Quartz	Hydrous mica	Kaolinite	Unchanged micas and felspar	Other minerals*
Hard purple	30.1	21.2	0.3	45	circa 4.0
Mild purple	28.2	23.5	2.7	41	" 5.0
Dry white	36.4	26.0	9.6	25	" 3.0
Buff stone	26.4	32.7	5.8	30	" 5.0

* Other minerals include fluor spar, topaz, apatite, tourmaline, rutile, all of which are present in small amounts in most samples.

Cornish stone is an important substitute for part of the felspar in the manufacture of porcelain, chinaware, fine earthenware and stoneware. Being less fusible than the best felspars, it is less liable to cause distortion in the kiln and both Cornish stone and felspar are often used simultaneously, particularly in glazes. It is a convenient source of silica, alumina and potash in suitable proportions to ensure a good glass-former which will, in the kiln, slowly dissolve other parts of the body and greatly increase its strength and density when cold.

The *pe-tun-tse* rock used by the Ancient Chinese porcelain-makers appears to have been a kind of china stone, resembling that found in Cornwall, but prepared for use by careful grinding and meticulous sedimentation in order to produce the most uniform material obtainable. The term *pe-tun-tse* (little brick) should not be applied to the crude rock.

MAGNESIUM-BEARING MATERIALS

DEVELOPMENTS in the iron and steel industry have been largely limited by the types of refractories which have to be used to line furnaces and other containers.

¹ Keeling, P. S., *Trans. Brit. Ceram. Soc.*, 53, 67, 1954.

The necessity of producing ferrous alloys free from acid contaminants led to the introduction of non-silicic refractories which were at the same time resistant to molten basic slag. The choice of a truly basic material which has a high refractoriness and is not unduly expensive is limited to compounds of magnesium and lime.

The principal *magnesium minerals* which occur in nature are:

Magnesium carbonate or *magnesite* (MgCO_3), forms white, grey, yellow or brown amorphous grains or hexagonal crystals having a hardness of 3.5–4.5 and a specific gravity of 2.8–3. Two varieties occur; a spathic or coarsely crystalline form and a dense crypto-crystalline variety.

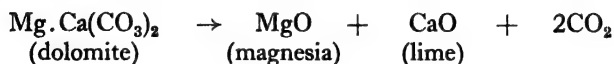
The spathic type of magnesite is found in Austria, Czechoslovakia, Russia, Washington, U.S.A. and Brazil. Compact magnesites occur mainly in Greece, Yugoslavia, Russia, Canada, the United States of America, and Manchuria, and are usually purer than the spathic type.

The principal impurity is free silica in the form of quartz, but there is always some associated lime and iron oxide, as a result of the ease with which the carbonates of magnesium, calcium and iron form solid solutions.

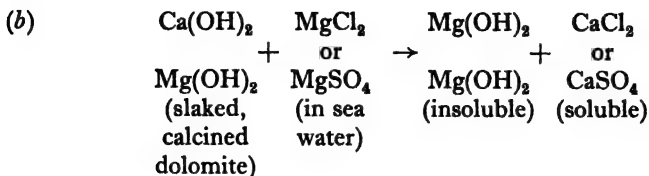
When the iron content is high the mineral is termed *breunnerite*, which implies a solid solution of magnesite (MgCO_3) with siderite (FeCO_3).

Magnesium hydroxide or *brucite*, $\text{Mg}(\text{OH})_2$, deposits occur in Canada and Nevada, but require purification before they can be used for the production of refractory materials.

Sea-water magnesia. At the onset of the second world war in 1939, nearly all the supplies of magnesium-bearing minerals were lost to British manufacturers who had relied mainly on the deposits in Austria and Greece. Steps were immediately taken to extract magnesia from sea water and the process has been so successful that a large proportion of the magnesia used for the manufacture of refractories in England at the present time is from this source. The basic idea of the process was not new, for as early as 1885 a small plant was operated on the South Coast of France to extract the 0.5 per cent of soluble magnesium salts from sea water. The chemical principle on which the separation depends is that soluble magnesium salts will react with a base and precipitate the almost insoluble magnesium hydroxide. Calcium hydroxide is the obvious reagent because of its availability and relative cheapness, but the yield of magnesia can be considerably increased by using dolomite as the precipitant. Dolomite is essentially the mixed carbonate of magnesium and lime which, on calcination yields the oxides of the metals thus:



Both the solid components slake readily with water to form hydroxides. Calcium hydroxide is sufficiently soluble to form a dilute alkaline solution which is the active precipitating agent for the precipitation of magnesium salts, and the magnesium hydroxide from the dolomite acts as a further source of magnesia. Hence when sea water is treated with a slurry of slaked, calcined dolomite a double decomposition reaction takes place which results in the formation of insoluble magnesium hydroxide and soluble salts of calcium. The series of reactions may be represented by the equations:

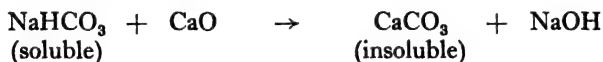


The precipitated magnesium hydroxide from the sea water along with the magnesia contribution from the dolomite is separated by sedimentation and filtration and is (theoretically) of sufficient purity for satisfactory use, though in practice, numerous side-reactions may take place which introduce impurities into the final product, and elaborate precautions have to be taken to reduce these to a minimum.

Dolomite is a commonly-occurring rock formation in the British Isles, and material of suitable quality is mined within twenty miles of the principal sea-water extraction plant at Hartlepool.

During the calcination of the dolomite, the impurities, such as silica, alumina, and iron oxide, are converted into insoluble calcium salts. In addition, contamination is introduced through the ash from the fuel used. Some unchanged calcium carbonate may also be present along with calcium sulphate arising from the sulphur in the coal. The overall result is to produce a proportion of insoluble calcium salts which are the principal impurities in the final product.

Calcium carbonate may also be introduced by the action of lime on any soluble bicarbonate in the sea water, thus:



This co-precipitation of calcium carbonate with magnesium hydroxide is avoided by treating the sea water, prior to the main reaction, with a small quantity of lime in a separate sedimentation tank. The above reaction takes place more readily than the formation of magnesium hydroxide, although calcium carbonate is inclined to form supersaturated solutions, especially when the water is cold. By careful control of conditions, however, little contamination from this source arises.

If the impurities due to side reactions are reduced to a minimum, sea-water magnesite can be produced with a total magnesia content, on a calcined basis, of more than 92 per cent. The lime content is always less than 3 per cent, although the amount is to some extent seasonable, being slightly higher in cold weather. Silica, mainly in the form of sand, is present in amounts of less than 2.5 per cent.

The analysis of some raw materials used in the manufacture of magnesia refractories are given in Table VI.XIV.

Dolomite or *Magnesian Limestone*, as the British deposits should be more correctly termed, is a mixed magnesio-calcium carbonate $\text{MgCa}(\text{CO}_3)_2$, which forms extensive rock formations. In its geological formation, two modes of origin are generally recognised. The primary form is the result of precipitation from solutions rich in both calcium and magnesium carbonates; such rock formations are uniform

in composition over large areas and are *true dolomites*. A much more common mechanism is where solutions rich in magnesium salts have filtered through a limestone (CaCO_3) rock, and caused extensive alteration in it, because magnesium ions are able to replace calcium in the lattice in considerable proportions, thereby producing true crystals which may be of variable composition, but are not a simple admixture of two carbonates. Secondary magnesian limestone may vary considerably in chemical composition, for the degree of alteration depends on the availability of magnesium solutions and the ease of penetration. Ferrous iron can also enter the lattice and replace calcium and magnesium ions, although if the percentage is not too high, the value of the rock as a refractory material is not unduly influenced.

TABLE VI—XIV. ANALYSES OF CALCINED MAGNESITES

	<i>Austrian</i>	<i>Grecian</i>	<i>Rhodesian</i>	<i>Indian</i>	<i>Russian</i>	<i>Sea water magnesites</i>
	per cent	per cent	per cent	per cent	per cent	per cent
Magnesia	80-90	90-95	85-95	85-95	85-95	80-90
Alumina	0-4	0-2	0-1	0-1	1-4	1-6
Ferric oxide	4-9	0-1	0-1	0-1	2-5	2-6
Lime	1-6	1-7	0-1	0-2	2-4	2-5
Silica	1-10	0-4	5-10	0-5	0-3	2-4

A belt of magnesian limestone outcrops in England and runs parallel to the Pennine Chain from Durham to Nottinghamshire. Similar samples occur in North and South Wales. The rocks are composed of interlocking crystals which are variable in size from a crypto-crystalline variety with particles of 0.01 mm. or less, to rocks with grains visible to the naked eye. Those portions of this rock which are rich in magnesium and low in impurities are valued for refractory purposes; less pure rocks are lightly calcined and used as lime for building purposes. So great and localised is the variation in chemical composition that refractory and inferior quality magnesian limestone are often extracted in the same quarry. Chemical analyses of some selected samples used for refractory and building purposes are shown in Table VI.XV.

TABLE VI—XV. ANALYSES OF MAGNESIAN LIMESTONES

	<i>Durham</i>	<i>Yorkshire</i>	<i>Derbyshire</i>	<i>North Wales</i>	<i>South Wales</i>
	per cent	per cent	per cent	per cent	per cent
CaO	32.0	29.5	30.3	31.7	30.2
MgO	19.7	21.0	19.8	19.0	19.5
FeO	—	0.4	—	0.1	—
Fe ₂ O ₃	0.4	0.4	0.6	0.2	1.0
SiO ₂	0.6	0.2	0.3	1.2	1.1
Al ₂ O ₃	0.5	1.4	1.0	0.8	1.2
Loss on ignition (mainly CO ₂)	46.8	46.1	47.1	46.5	46.8

Other magnesium-bearing materials include the important groups of magnesium silicates; serpentines, talc, forsterite, spinel, cordierite and vermiculite.

Serpentine is essentially a mixture of fibrous needles of *chrysotile* and *antigorite* which have the formula $3\text{MgO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. It is of frequent occurrence, as it is a common alteration product of rocks rich in magnesium and iron. In only a few localities, however, does it form extensive deposits free from excessive quantities of other minerals. A particularly valuable source is in the Shetland Isle of Unst, which has been called the 'green' isle because of the colour of the outcropping serpentine.

The mineral is of importance as a stabiliser of dolomite for refractory purposes and as a raw material in the manufacture of forsterite refractories.

Talc or *steatite* ($3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$), is of value in the manufacture of ceramic insulators of the electrical low-loss type, also of forsterite refractories and in the tile industry. It occurs in many localities although 65 per cent of the world's supply comes from Canada and the United States. Two forms are recognised, (a) soapstone, steatite or crypto-crystalline talc, and (b) true talc which is composed of much larger crystallites.¹

Talc deposits, mined on a commercial scale, are extensive and may be up to 800 ft. thick. The *principal impurities* are carbonate rocks (magnesite, breunnerite), chlorites and quartz. Egyptian steatite is used in considerable quantities in this country and Gad² gives the following analysis for a talc-carbonate rock from this locality:

	per cent		per cent
SiO_2	31.04	TiO_2	0.08
MgO	35.15	CaO	0.23
Al_2O_3	0.54	K_2O	0.01
Fe_2O_3	3.02	Na_2O	0.01
FeO	4.32	Cr_2O_3	0.33

Loss on ignition 25.18 per cent

The relatively high figure for magnesia and the low content of alkalis suggest that this sample would be of value as a refractory, but in general, talc for the electrical and tile industry should have less iron and a much lower loss on ignition.

Asbestos is a form of magnesium silicate which occurs in a fibrous form. The principal types of minerals in asbestos have been detailed by Williams³ who has also outlined the properties of each type. The most common form of asbestos contains fibres of *chrysotile*, $3\text{MgO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. Some authorities term this type *fibrous serpentine*, and reserve the term asbestos for those deposits containing a true *amphibole*. These latter may be of three types: (a) the *tremolite-actinolite* series $(\text{OH})_2\text{Ca}_2(\text{Mg}, \text{Fe})_5\text{Si}_8\text{O}_{22}$; (b) fibrous *anthophyllite* $(\text{OH})_2(\text{Mg}, \text{Fe})_7\text{Si}_8\text{O}_{22}$; and (c) *riebeckite* or *crocidolite* $(\text{OH})_2\text{Na}_2\text{Fe}_3^{2+}\text{Fe}_2^{3+}\text{Si}_8\text{O}_{22}$. Minerals of this last group form longer fibres than the mineral chrysotile, but, on the whole, they tend to be less refractory because of adsorbed alkali ions. The chief producing countries of asbestos are Canada, Southern Rhodesia, South Africa and Russia.

¹ Steatite is dehydrated at a lower temperature than talc; it also forms clino-enstatite (p. 336) more rapidly.

² Gad, G. M., *Trans. Brit. Ceram. Soc.*, 51, 429, 1952.

³ Williams, A. E., *Mech. Wld. Monogr.*, No. 47 (Emmott, London, 1948).

Vermiculites are essentially hydrated magnesium silicates although other cations are usually present in the mineral lattice (see p. 157). This group of minerals resemble soft mica in appearance, but exfoliate when heated. The expanded mass is of value as a thermal insulator and is becoming important as a light-weight filler. Vermiculite is frequently present in small amounts in soil clays, but extensive workable deposits are limited. The principal source is in Montana, U.S.A., but potentially good formations have been reported as existing in Tanganyika, Africa, Australia and India.

Olivine is a naturally occurring magnesium-iron orthosilicate $(\text{Mg,Fe})_2\text{SiO}_4$ containing varying amounts of magnesium and iron. It is a constituent of some igneous rocks, e.g. peridotite and dunite, which is almost a pure olivine; it is also a major component in some basalts and dolerites.

Olivine rocks are found in Cornwall, the Shetland Isles, Northern Ireland and many localities abroad, but it is usually extensively altered to serpentine.

Those minerals which contain less than 5 per cent of ferric oxide are used in the preparation of *forsterite* refractories. Forsterite is the magnesium end-member of the olivine series but it rarely occurs in the pure state in nature. Serpentine and talc are also used in the manufacture of refractories, but, unlike olivine, they shrink considerably on firing, even after being pre-calcined. They are, however, usually much purer than natural olivines especially with regard to their iron content.

Cordierite, $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$, is rare as a natural mineral, but artificial products of the same composition are of great commercial interest because their coefficient of expansion is less than that of vitreous silica and they possess great thermal endurance. Artificial cordierite is made by heating a mixture of china clay or fireclay with magnesite, steatite or olivine. The iron content should be kept as low as possible.

*Spinel*s form a group of mixed oxides of which the mineral spinel $\text{MgO} \cdot \text{Al}_2\text{O}_3$ is typical. They are described in detail in the section on chrome-ores and their structure has been considered in Chapter IV.

Most magnesium compounds decompose on heating and either combine with other substances of an acidic character (e.g. $2\text{MgO} + \text{SiO}_2 = \text{Mg}_2\text{SiO}_4$) or crystallise as *periclase* MgO .

CALCIUM-BEARING MINERALS

CALCIUM carbonate, CaCO_3 , is a widely distributed rock formation for it is the essential component of chalk, limestone and marble. In addition, calcium carbonate occurs as Iceland Spar, in crystals of calcite and aragonite and as shells and allied organic structures.

Pure calcareous limestone is used to a very small extent as a refractory material—because of the instability of the calcined product (lime)—although a method of stabilising it has been described by Williams.¹ Lime is, however, an important base in the manufacture of glass, sand-lime bricks and mortar; chalk is used in the manufacture of some kinds of bricks and pottery, and whiting (finely-ground calcium carbonate) is an important ingredient in some glazes.

¹ Williams, A. E., *Trans. Brit. Ceram. Soc.*, 50, 215, 1951.

Calcium sulphate (gypsum, anhydrite and selenite) occurs in massive form near Newark. Gypsum is chiefly of importance as the source of plaster of Paris, from which are made the *plaster moulds* so extensively used in pottery manufacture. The gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is heated to a temperature of about 107°C . with constant stirring until it 'boils' and evolves some of the combined water present, forming plaster ($2\text{CaSO}_4 \cdot \text{H}_2\text{O}$ or $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$). This material is ground to a 'superfine' powder and is then ready for use.

CHROME ORES

CHROME ores have been used in the manufacture of neutral fire-bricks to separate courses of basic and acidic refractories in metal-melting furnaces. The development and increasing use of chrome-magnesite bricks has drawn attention to the composition of these rocks and they are now important refractory materials. The mineral chromite, FeCr_2O_4 , is the only significant source and its principal occurrence is in Southern Rhodesia where it forms lenses or bands which are either solidified intrusions or a highly crystallised, compacted sediment. The principal impurities are iron and titanium minerals, but the chromite grains are often of very variable composition due to solid solution and may contain appreciable amounts of aluminium and magnesium. Chrome ores occur in massive form in many other localities; and the main chemical ingredients of suitable rocks are:

Chromic oxide	Cr_2O_3	between	33–45 per cent
Aluminium oxide	Al_2O_3	,,	14–27 per cent
Magnesium oxide	MgO	,,	10–20 per cent
Iron oxide	FeO and Fe_2O_3	,,	10–15 per cent
Silica	SiO_2	less than	7 per cent
Calcium oxide	CaO	,,	1.5 per cent

Despite the apparent complexity of their composition, chrome ores contain one principal mineral type, *spinel* and only small amounts of impurities.

The compositions and types of various spinels have been described in Chapter IV (p. 193), where it was shown that a complex system of solid solutions exists with the general formula $\text{R}^{2+}\text{O} \cdot \text{R}_2^{3+}\text{O}_3$ where R^{2+} is any divalent cation, such as Mg or Fe^{2+} but not Ca, and R^{3+} is a trivalent cation such as Al, Cr, or Fe^{3+} .

The spinel grains which occur sometimes as octahedral crystals, but more often in massive form with a granular and compact structure, are usually brownish in colour due to the presence of iron. They are brittle with a hardness of 5.5, a specific gravity of 4.3–4.5 and a high melting point.

The *impurities* are present in the form of gangue which holds the spinel grains together. These impurities include *quartz*, *pyroxenes* and *felspars*, but are chiefly *serpentine*, $3\text{MgO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$.

The principal sources of chrome ore are Rhodesia, Sierra Leone, Transvaal, India, the Isle of Unst (North Scotland), Turkey, Greece, Yugoslavia, Russia and the Philippine Islands.

A material with a low porosity and large unfissured grains of spinel is preferred for refractory purposes.

TITANIUM-BEARING MINERALS

ALTHOUGH a small percentage of titanium compounds is invariably present in most clays and sedimentary rocks, there are only a few known sources of rich titanium-bearing rocks.

The chief titanium minerals are as follows:

Rutile, TiO_2 , is a titanium oxide occurring as reddish-brown, yellowish or black tetragonal crystals, with a hardness of 6-6.5 and a specific gravity of 4.2. As it is practically indestructible, it is one of the commonest heavy detrital minerals in clays and is of very wide occurrence. It also occurs in massive form. It is the stablest form of titania and is readily formed from other oxides on heating.

Brookite is a titanium oxide of more limited occurrence; it is found as brown, red, or blackish orthorhombic crystals, with a hardness of 5.5-6 and a specific gravity of 4. It is almost as durable as rutile and has been isolated on a commercial scale from Arkansas red clays.

Anatase is a titanium oxide occurring as slender brown, blue or black tetragonal pyramids, with a hardness of 5.5-6 and a specific gravity of 3.83-3.95. It is of somewhat limited occurrence, although Brindley¹ has reported that it is the principal variety of titania in British fireclays.

Ilmenite, $\text{FeO} \cdot \text{TiO}_2$, is a very common detrital mineral, consisting of a mixed oxide of iron and titanium; it occurs as black tetragonal crystals, with a hardness of 5-6 and a specific gravity of 4.5-5.0. In the massive form it is one of the principal sources of titanium oxide for use in refractory materials.

Sphene, CaTiOSiO_4 , is a calcium titanite and silicate which occurs as brown, green, yellow, or black monoclinic crystals, having a hardness of 5-5.5 and a specific gravity of 3.54. It also occurs in massive form.

Leucoxene is a variety of sphene produced by the alteration of ilmenite and other titanium-bearing minerals.

Titania is the principal ingredient of bodies when a low dielectric loss is required, as in radio work; it is also used to some extent as a refractory, as a high temperature lute or cement and as an opacifier in glasses and glazes.

Titania is extracted from naturally-occurring sands, found principally in India and Australia, where it occurs as ilmenite, or rutile. The minerals may be purified by separation with heavy liquids (p. 271) and fluidisation.

ZIRCONIUM-BEARING MINERALS

ZIRCONIUM occurs in two forms in nature, as:

(a) the oxide ZrO_2 (*baddeleyite*) which is found principally in Brazil in the massive form or as concretionary pebbles or nodules. It forms monoclinic crystals, unstable at high temperature, with a melting point of about 2700° C., a high refractive index (*circa* 2.15), and a specific gravity of 5.7-6.0.

(b) The silicate, *zircon* (ZrSiO_4), which occurs as grey, yellow, green or reddish-brown tetragonal crystals with a hardness of 7.5, a specific gravity of 4.7, and a melting point of about 2550° C. in detrital deposits, principally monazite sands.

¹ Brindley, G. W., loc. cit., p. 284.

The entire British supplies of zircon come from the monazite beach sands in Travancore, India or Australia. The sands contain up to 60 per cent of zircon, but when washed, yield a fine-grained sample up to 99.5 per cent pure. The chief impurities are titanium compounds, quartz and feldspar.

Zircon is used as a refractory material; it is very resistant to the attack of coal ash and molten metals at high temperatures. Although it begins to dissociate at about 1600° C. into zirconia and free silica, it can be used at considerably higher temperatures without serious deterioration.

Monazite sands are also important sources of other ceramic oxides and a typical analysis shows 5 per cent of monazite (phosphate of cerium, lanthanum, ytterbium with thorium, ThO_2), 20 per cent of ilmenite or rutile and 15 per cent of zircon or zirconia. The various components can be purified by heavy liquid separation.

BERYLLIUM-BEARING MINERALS

Beryllia, BeO , has many advantages as a refractory material and is being used on an increasing scale in the United States. Largely because it is considered a health hazard, it has had only limited application in this country.

The principal source is beryl ($3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$), which is associated with the massive feldspars in Brazil, India and the United States. The natural mineral contains 10–12 per cent of BeO , so that purification is necessary; the mineral is first concentrated by froth-flotation methods and after the ore has been partially decomposed by heating it above 1000° C. with lime, the beryllia is extracted by hot sulphuric acid.

Beryllia is highly refractory (M.P. 2570° C.), yet it readily sinters at about 1300° C. to form a mass of low porosity with excellent resistance to thermal shock and with high electrical resistance at elevated temperatures. It is chiefly used for laboratory crucibles and gas-turbine blades, but it has great potential value as a super-refractory and it also confers desirable properties when it is a component of glazes and porcelains.

CARBON

ALTHOUGH most of the carbon used in the ceramic industries is now manufactured, naturally-occurring *graphites* are still highly valued for special applications.

Graphite probably originates through the metamorphism of carbonaceous material of sedimentary origin and is frequently found in coal-bearing regions where there has been volcanic intrusion. There is a small amount of graphite mined in Cumberland, but the principal sources are in Ceylon, Norway, Korea, Austria and the United States. The quality of the graphite is of major importance and is governed principally by the size of the flakes. Ceylon graphite with large flakes is eminently satisfactory for the manufacture of crucibles and some other refractory shapes.

For most purposes, however, a synthetic form of graphite is nowadays preferred, and this is prepared by heating coke of low ash-content mixed with tar or pitch, in the absence of oxygen. The temperature of firing determines the texture of the product and the size of the crystallites. Graphite for carbon refractories is

imparts and the latter to give strength to the unfired shapes. *Flint* is added to reduce the shrinkage and to increase the porosity and the silica content. A *flux*, such as *china stone* or *felspar* is also introduced, which forms a glass in the fired body and therefore imparts strength, density and the power to ring when struck. In recent years *talc*, *pyrophyllite* and various other silicates have been included in earthenware bodies used for glazed wall- and floor-tiles.

For a slightly inferior fine earthenware, a mixture of *red-burning clay* and *chalk* is sometimes used. The chalk combines with the iron compounds in the clay and, if skilfully proportioned and fired, it produces a white body. This kind of hollow ware is seldom made in England, but the process is used in the manufacture of some white bricks.

Various blue colours may also be used to destroy the yellow colour of some burned clay and in this way some otherwise unsuitable clays may be utilised for fine earthenware manufacture.

The average composition of the raw materials in British fine earthenware bodies to be fired between 1100° C. and 1160° C. is:

	Range	Average content
Ball clay	20-45 per cent	25 per cent
China clay	25-40 per cent	25 per cent
Flint	20-35 per cent	35 per cent
China stone or felspar	7-15 per cent	15 per cent

Sanitary earthenware is of two kinds:

(i) That with a porous body, sometimes covered with a white or coloured engobe and a glaze, or with a salt glaze. This is a true earthenware.

(ii) That with a vitreous body like stoneware but not so dense. It is usually made of *china clay*, *ball clay* and *flint* with about 15 per cent of *Cornish stone* and 10-15 per cent of *felspar* (see *Stoneware*, p. 340).

CHINAWARE AND PORCELAINS

Chinaware and Porcelains are made of mixtures of various white-burning clays and fluxes of such a nature and in such proportions as will produce a dense, vitreous and translucent body. The temperature of firing of these bodies is usually much higher than for earthenware, being in the range 1260-1400° C. The term *porcelain* includes a great variety of wares all of which are translucent and are, in this way, distinguished from stoneware. What is usually termed *true* or *hard porcelain* contains a large proportion of clay and forms one end of a series, the other end being *soft porcelain*, which consists chiefly of an opaque glass and may contain very little clay. *Bone china* differs from other porcelains in containing bone ash, and is almost exclusively made in England. It is true porcelain though not usually regarded as such. The paste used for bone china bodies is difficult to shape because of its low plasticity; in recent years this has been improved by adding a small proportion of bentonite (see p. 309).

Chinaware is made of *china clay*, *ball clay*, *flint*, *Cornish stone*, *bone ash*, *felspar* and other fluxes. It owes its translucency largely to the formation of a glassy binding

material formed by the combination of the fluxes and the silica. Such ware usually varies in composition between the following limits:

1.15 to 8.33 ($R_2O + RO + Al_2O_3$); 1.97 to 9.08 SiO_2 ; 0.35 to 2.67 P_2O_5

True (or *Ideal*) *porcelain* should consist of a mixture corresponding to a core or skeleton of matted crystals of *mullite* ($3Al_2O_3 \cdot 2SiO_2$), enclosed in a fusible glass rich in silica, which binds the other particles together. Thus porcelain is made of clays and fluxes heated to a temperature sufficiently high to form a felted mass of mullite needles bonded with a glassy cement.

There are at least six distinct types of porcelain with many intermediates and the clays used for one type are not necessarily suitable for another.

(1) **Hard-paste porcelain**, including *porcelaine dure*, *Halle porcelain*, and *Berlin porcelain*,¹ corresponds approximately to the composition

0.2 to 0.3 ($R_2O + RO + R_2O_3$); 4.2 to 4.8 SiO_2

It is made of *kaolin* (china clay), *orthoclase felspar* and *flint* or *quartz*. Hard porcelains are resistant to sudden changes in temperature and to most acids.

(2) **Soft porcelain** or *porcelaine tendre*, corresponding to the formula

0.4 to 0.45 ($R_2O + RO + R_2O_3$); 4.8 to 5.3 SiO_2

This material is really a complex glass and not a true porcelain. The soft porcelains are so rich in alkalis that a considerable portion of the raw material is *fritted*, i.e. pre-melted and then crushed, before being mixed with the rest. Because of the excessive amount of liquid formation at the temperature of firing, serious distortion of the ware may occur unless close control is maintained. The manufacture of soft porcelain in several well-known factories was never permanently profitable; the 'loss on firing' was so great. This product was developed in France where it became known as *porcelaine de Reaumur* and is still manufactured in the Limoges area.

(3) **Sèvres porcelain** is made essentially of a mixture of clays and fluxes which are intended to form a special kind of glass, the chief materials being *white-burning kaolins*, *felspar* and *quartz*. Sèvres porcelain corresponds approximately to the formula

0.30 to 0.35 ($R_2O + RO + R_2O_3$); 2.8 to 3.5 SiO_2

The *Meissen* and *Viennese* porcelains are similar in composition to that of Sèvres.

(4) **Chinese and Japanese porcelains** vary so greatly in composition and are so complex in character owing to the very impure materials used, that they can be scarcely said to correspond to any formula, though they are chiefly within the following limits:

Japanese 0.3 to 0.4 ($R_2O + RO + Al_2O_3$); 6.2 to 7.4 SiO_2

Chinese 0.4 to 0.45 ($R_2O + RO + Al_2O_3$); 5.5 to 6 SiO_2

Sèvres imitation of

Oriental porcelain 0.37 ($R_2O + RO + Al_2O_3$); 5.15 SiO_2

Seger's imitation of

Oriental porcelain 0.36 ($R_2O + RO + Al_2O_3$); 8.55 SiO_2

¹ Most chemical and laboratory porcelain resembles Berlin porcelain and is based on the same formula with slight modifications due to the composition of the materials.

felspar, etc., and great attention paid to the grain size of the components, the reactions proceed at suitable rates and enable satisfactory results to be obtained repeatedly with hard porcelain, but with much greater risk of loss when soft porcelain wares are made.

H. Hope¹ has given the following summary of the effect of various fluxes upon white porcelain mixtures:

Lime, or its equivalent, gives a strong porcelain with moderate shrinkage and only a slight tendency to blister, but the colour of the ware is rather poor.

Magnesia tends to cause blisters, but if less than 0.1 equivalents are present, this is not serious; the colour of the ware is usually good.

Strontia has little tendency to blister and gives a strong ware with high porosity and low shrinkage; the colour of the ware is fairly good.

Barium oxide gives a weak body, with excessive shrinkage and blistering. The translucency of the ware is better than other fluxes, but the colour is poor.

Zinc oxide produces ware of a very good colour, even in small quantities, but with more than 0.05 equivalents there is sometimes a bluish or greenish tinge. With 20 per cent of felspar, zinc oxide gives a good strong body, but with more than 0.02–0.03 equivalents of zinc oxide the ware tends to opacity and there is a tendency to 'shivering'.

Soda and *potash*—preferably in the form of felspar or Cornish stone—are the best fluxes for porcelain. Parmelee and Amberg² have found that quartz is much more readily soluble in soda-felspar than in potash-felspar and that solution commences at a lower temperature (1350° C. as against 1400° C.).

TABLE VI—XVII. CHEMICAL COMPOSITION OF PORCELAINS

Porcelain	Silica	Alu- mina	Ferric oxide	Potash	Soda	Lime	Mag- nesia	Titan- ium oxide	Borax	Loss on ignition
Sèvres (1848)	59.2	35.2	—	3.2	—	3.2	—	—	—	—
Dental A	68.2	16.7	trace	10.1	2.3	—	—	0.23	—	2.5
Dental B	68.1	2.2	—	6.9	10.1	0.8	—	trace	10.6	1.2
Dental C	69.6	11.3	0.3	11.8	1.7	2.4	—	0.2	0.3	—
Meissen	58.5	35.1	0.8	5.0	—	0.3	0.6	—	—	—
Vienna	59.6	34.2	0.8	2.0	—	1.7	1.4	—	—	—
Berlin	64.3	29.0	0.6	3.6	2.7	0.3	0.5	—	—	—
Chinese	70.0	22.2	1.3	3.6	2.7	0.8	—	—	—	—
Marquardt's	61.6	30.0	1.56	3.26	—	3.56	—	—	—	—

It is probable that felspar serves two separate purposes in porcelain: (i) as a solvent of the quartz; and (ii) as a liquid which penetrates the interstices in the felted 'skeleton' and when cold, cements the other particles together, at the same time sealing the pores.

Table VI.XVII shows the chemical composition, and Table VI.XVIII the mixtures used for various porcelains.

¹ Hope, H., *Trans. Amer. Ceram. Soc.*, 11, 494, 1909.

² Parmelee, C. W. and Amberg, C. R., *J. Amer. Ceram. Soc.*, 12, 699, 1929.

TABLE VI—XVIII. MIXTURES USED FOR VARIOUS PORCELAINS

Porcelain	Stèvres	Berlin	Chinese	Seger	Bone China			Dental			American China*		Chemical†	Parian Ware		
					A	B	C	A	B	C	Hotel	Household		A	B	C
Kaolin	38	77	47	13.0	33-35	26	30	4	—	—	35	24	} 80	33	16	40
Ball clay	—	—	—	15.5	—	—	—	—	—	—	7	28		—	—	—
Felspar	38	23	15	30.0	15-19	—	—	81	61	12	22	13	10	67	33	58
Cornish stone	—	—	—	—	—	30	35	—	—	—	—	—	—	—	—	—
Flint	—	—	—	—	10-14	—	—	15	29	60	35	35	—	—	—	—
Quartz	24	—	38	41.5	—	—	—	—	—	—	—	—	10	—	51	2
Bone ash	—	—	—	—	32-42	44	35	—	—	—	—	—	—	—	—	—
Sodium carbonate	—	—	—	—	—	—	—	—	2	8	—	—	—	—	—	—
Borax	—	—	—	—	—	—	—	—	1	11	—	—	—	—	—	—
Calcium carbonate	—	—	—	—	—	—	—	—	5	1	1	—	—	—	—	—
Potassium carbonate	—	—	—	—	—	—	—	—	2	8	—	—	—	—	—	—

* American china ware is of slightly different composition from that of British ware. More alkali in the form of felspar or nepheline syenite is used along with a little lime or magnesite.

† Most chemical and laboratory porcelain resembles Berlin porcelain and is based on the same formula with slight modifications due to the composition of the materials.

The *Bone ash* used in the manufacture of bone china is prepared by calcining the bones of oxen, and consists essentially of tri-calcium phosphate. The addition of bone ash to clays imparts translucency, even in porous bodies which have not been fired to the vitrification point.

The composition of porcelain depends largely on the temperature to which it is fired. For example, 28 per cent of felspar is sufficient if the body has to be fired at 1400° C., but this has to be increased to 35 per cent at the expense of other ingredients if the firing temperature is reduced to 1300° C.

Parian ware, though usually included as a porcelain is, strictly, a very fine stoneware as the articles made of it are vitreous, but not translucent. The Parian ware originated by Copeland and Garret of Stoke-on-Trent about 1845 was composed of one part of *china clay* and two parts of *felspar*. The French Parian ware is largely composed of *frit*, *kaolin* and *felspar* and sometimes contains *flint glass*.

STONEWARE

Stoneware resembles porcelain in texture, being vitreous and glassy, but *plastic clays* are used in its manufacture instead of kaolins. Consequently, stoneware bodies are much easier to shape by moulding than are porcelain ones; they are also less fragile and less brittle. The chief difference between stoneware and porcelain is the translucency of the latter, although porcelains vary in themselves in their degree of translucency. Many articles described as fine stoneware are really non-translucent, under-fired porcelains, but are not regarded as such because of their colour and general appearance.

Chemical stoneware has a particularly high resistance to many chemicals and is of great industrial and technical importance.

Sometimes the term stoneware is, wrongly, applied to *glazed earthenware* used for sanitary purposes such as drain-pipes, gullies and traps. This differs from stoneware in having a porous body and relies for its impermeability solely on the glaze, whereas true stoneware has an impermeable body with or without a glaze.

One of the most interesting kinds of stoneware is Josiah Wedgwood's *Jasper ware* in which barium sulphate (barytes) is the chief flux: the colour is due to chromium oxide (green ware) or to cobalt oxide (blue jasper). This ware is not glazed but has a slightly glossy surface.

The chief requirement of stoneware in general use is its impermeability to liquids. Its colour is usually of minor importance and this enables cheaper and less pure clays to be used in its production; but, for fine stoneware, white-burning clays, such as *plastic kaolins* and *ball clays* must be used, though occasionally a mixture of fireclay and china clay is quite satisfactory, particularly for some vitreous sanitary ware.

Stoneware may, therefore, be regarded as similar to earthenware which has more natural fluxes or to which additional fluxes have been added, to produce a dense, vitrified body when fired at a suitable temperature.

Coarse stoneware is chiefly made of bastard (siliceous) fireclays which contain sufficient fluxes to need no further addition; in some cases, a small proportion of a suitable flux (usually chalk but sometimes magnesia or a cheap felspar) is added.

Fine stoneware and **chemical stoneware** is made of kaolin, ball clay or one or other of these with a coarser refractory clay (e.g. fireclay), sufficient china stone or felspar and flint or fine sand. These are added in proportions sufficient to produce the kind of body required.

When a stoneware is required to have a high resistance to sudden changes in temperature (e.g. some chemical ware) it is usual to include a moderate proportion of *talc*, *mica* or *magnesia* to act as a flux, reduce thermal expansion and to impart thermal stability.

The outstanding advantages of stoneware over porcelains are: (i) ease in moulding; (ii) toughness of the fired ware; (iii) less loss (rejects) in manufacture; (iv) cheaper raw materials, especially clays; and (v) smaller total cost. These advantages also apply to many technical porcelains which, as previously stated (p. 336), are better described as stoneware than as porcelain.

Coloured bodies may be produced:

(i) By using clays which, when suitably fired, have the desired colours, e.g. red-burning clays for terra-cotta; these usually owe their colour to the presence of iron-bearing minerals such as haematite.

(ii) By adding a suitable colouring agent (or stain), such as those used for engobes and glazes (p. 353).

(iii) By firing under reducing conditions which reduce ferric compounds to the ferrous state and produce dark blue, purple or very dark brown coloured substances.

The addition of a colouring agent to the whole of the body is usually too expensive and, where practicable, it is cheaper and, in many cases, equally satisfactory to apply a coloured engobe glaze or veneer to those parts of the article which are visible when it is in use. Such examples are sand-faced or veneered building bricks where the surfaces to be exposed are covered with a coloured sand or clay; coloured, glazed sanitary ware and glazed fireclay drain-pipes are also of this type. The colouring agents are chiefly cheap oxides which, in the kiln atmosphere, produce a pleasing appearance on the fired body.

ENGOBES

Engobes are intermediate in composition between clay bodies and glazes. They are vitreous but less glassy than glazes and are used principally:

(a) To hide the colour of the body and to prevent the top glaze, which is much more fusible, dissolving some of the coloured body and thus becoming coloured itself.

(b) As a material with a thermal expansion intermediate between that of the body and the glaze. A highly desirable glaze which would not otherwise adhere to the body may be used if one or more layers of engobe are fired on to the body previously.

Engobes vary considerably in composition but usually consist of *china clay*, *ball clay*, *flint*, *Cornish stone* or *felspar* and *whiting* (crushed *calcium carbonate*). The thermal expansion can be adjusted between wide limits by varying the proportions of

these constituents. Coloured engobes are produced by adding suitable oxides to the mixture (see p. 353).

GLAZES

Glazes are applied to many kinds of clay ware to give a glossy finish which seals the body and at the same time provides a smooth and matt or a brilliant surface. They resemble glasses in structure and texture, but their composition is adjusted to ensure a suitable but not complete amount of vitrification and a more viscous fluid. Glazes must also adhere closely, strongly and uniformly to the ware or engobe.

Glazes are made for use at all temperatures from about 600° C. to 1500° C. according to the articles to which they are applied. They are also made to have glossy, matt, dull or other surfaces, according to requirements and, in some cases to be highly resistant to acids and other liquids and corrosive gases.

Semi-conducting glazes are required in some industries to reduce radio interference and to control the voltage gradient over large insulators. They are usually made by mixing metallic oxides with a felspathic glaze and firing the coated articles under reducing conditions, so that a film of metal is produced and this has an electric conductivity sufficient for the purpose.

Lustre-glazes which show a metallic lustre are highly decorative; they are made in a manner similar to semi-conducting glazes.

Broadly, glazes are composed of groups of materials:

- (i) Bases corresponding to alkali and alkaline earth oxides.
- (ii) Alumina.
- (iii) Silica and other 'acid' radicles.
- (iv) Other oxides added to produce certain effects, such as opacifiers, colorisers, etc.

Instead of using the simple oxides, it is more satisfactory to use compounds containing the components (e.g. feldspar and china stone) which melt readily and act as solvents for the other ingredients. In most glazes, the larger the proportion of alkalis and other bases, the more fusible will be the glaze and the brighter the colours produced by pigments, although this does not apply to all glazes.

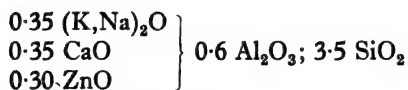
It is important in glazed ware to ensure that the coefficient of thermal expansion of the body should be similar to that of the glaze, otherwise *peeling* (when the body has a greater expansion than the glaze) or *crazing* (when the glaze has the greater expansion) will occur. A high content of alkali, particularly sodium, usually produces a glaze of large thermal expansion but replacement by calcium or magnesium reduces this tendency. The ratio of RO:R₂O has a particularly great influence on the nature and many properties of glazes. Variations in it cause great differences in the fusibility, transparency, opalescence as well as the liability to craze. In this respect, the RO:R₂O ratio has a much greater effect than a similar change in the proportions of alumina and silica.

Glazes may be divided—so far as their chemical composition is concerned—into:

- (a) **Alkaline glazes**, consisting chiefly of silicates of potash and soda; the most important of these are (i) salt glaze for stoneware; and (ii) some of the unstable

glazes occasionally used for ornamental ware and enamels. These, although easy to apply, are usually slightly soluble and not so resistant to wear.

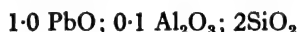
(b) **Felspathic glazes**, consisting of silica and alumina, with alkaline or alkaline earth bases. The main component in this type of glaze is feldspar, but flint, whiting and sometimes a little clay is also added; in this way the thermal expansion can be controlled. Felspathic glazes are relatively cheap, but require extreme care in use. One of the best-known examples is *Bristol glaze* which is used on cheap earthenware and on some white sanitary ware. Its composition corresponds to:



The zinc oxide is added as an opacifier.

(c) **Lead glazes**, which may consist of (i) a simple lead silicate $\text{PbO} \cdot 2\text{SiO}_2$, or (ii) a glaze similar to felspathic glazes, but having the melting point reduced and the appearance improved by the addition of lead compounds.

Lead glazes may be made of red lead and flint, but are often improved by the addition of a little clay, whiting or other flux. A well-known mixture corresponding to



can be used on ware fired at 650°C . (cone 019); with more silica a much higher temperature is required to produce a clear glaze.

In lead glazes containing soda, potash and lime (or any of these) the maximum amount of alumina which can be accepted depends on the $\text{RO}:\text{R}_2\text{O}$ ratio, but with the alumina equivalent between 0.1 and 0.5 good clear glazes can usually be obtained. With a larger amount of alumina, semi-glazes and matt glazes are produced.

Like other glazes, those containing lead must be adjusted to suit the ware to which they are applied. For a reason not fully understood, however, lead glazes do not require such rigid control in use as do other types.

Some lead compounds in glazes are highly poisonous and their use is only permitted if they conform to certain Regulations under the Pottery Acts. Their poisonous nature may be largely obviated by converting them into insoluble silicates.

Lead compounds impart high lustre to glazes in which they are present. This is because lead atoms can take part in a network structure of silica and in so doing become greatly distorted or polarised; in this form they increase the refractive power of the glaze enormously. Because lead can and does take part in network structures it is not correct, when calculating glaze formulæ, to regard it as a RO type oxide.

(d) **Leadless boric acid glazes**, were developed during the Second World War, when lead supplies were in short supply. Borax, sodium borate, and boric acid are valuable constituents of glazes, because they have low melting points, readily form a glassy network and boron oxide can act as either an alkaline or as a basic component. Unlike silica, the greater the proportion of boric acid in a glaze, the lower will be its melting point and as this component also reduces the thermal expansion, it is a valuable additive.

Borates are usually highly soluble and for this reason they cannot be used, as such, in glazes which are applied in a watery medium. The soluble components of a glaze are *fritted* prior to use to convert them into an insoluble form. The *frit* is prepared by fusing together the soluble components and other low melting-point compounds; these include felspar, whiting, Cornish stone and flint. After being quenched, the frit is crushed and finely-ground before being added to the other components which make up the glaze composition.

Frits are also used when the components of a glaze have a wide range of melting point or are slow to react with one another. By fusing the compounds together prior to applying them to the body, absolute uniformity in the glaze is assured.

Borax is sometimes used alone as a glaze in a similar manner to salt (see p. 342). Some cheap, glazed clay-ware is prepared by throwing borax into the kiln during the final stages of the firing process. The borax combines with the clay body to form a complex sodium boro-silicate, which has the advantage of being much more insoluble than the compounds produced during salt-glazing.

(e) **Loam glazes** are composed of a fusible clay to which felspar, whiting, flint or similar fluxes are added. They are chiefly used for slip-ware, art-ware and 'peasant' ware and are of common use in some countries.

(f) **Enamels**, which are ordinary lead or felspathic glazes rendered opaque by the addition of tin oxide or other opacifying agent. (Unfortunately, the term *enamel* is also used for transparent glazes applied to metals, but in the pottery industry its use is largely confined to opaque glazes.)

In order that it may be satisfactory, a glaze must possess three characteristics: (i) it must have the desired transparency or opacity and colour; (ii) it must be perfectly adapted to the body or ware to which it is applied so as to avoid crazing or peeling; (iii) it must possess a suitable fusibility in order that it may mature at a convenient temperature which is also suitable to the ware to which the glaze is applied.

These characteristics are secured by suitably modifying the chemical composition of the glaze mixture. All these characteristics are equally important and yet, in some cases, they are incompatible, so that various compromises must be effected. An increase in transparency is usually obtained by making the glaze more fusible or by reducing the proportion of non-fusible matter in it. The adhesion of a glaze to the ware may sometimes be increased by adding clay (though this may make it less transparent), by making it more fusible (though this may cause 'crazing'), or by varying the proportions of the various minerals in such ways as previous experience may suggest.

The different constituents which are used in glazes and engobes play a large part in determining the nature of the fired mixture. They are as follows:

Silica is used in glazes to supply the chief acid radicle and also to regulate the temperature at which a glaze will mature. An excess of silica which remains unaltered in the glaze, decreases its transparency and prevents complete fusion except at a higher temperature. On the other hand, a deficiency of silica reduces the ductility of a glaze and imparts a tendency for it to boil and blister.

Silica reduces the expansion of a glaze, but at the same time increases the vitrification temperature. It is added in the form of (a) free silica, usually in the form of crushed flint, or (b) a silicate combined with alumina in the form of kaolinite $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ or as feldspar $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$.

Alumina sometimes acts as a base in glazes, but it does not influence the fusing-point to any great extent. Its chief value is to permit considerable variations in the composition and firing of the glaze without greatly altering the physical properties; it is particularly useful in preventing crystallisation. It also acts as a clarifier and is especially necessary in lime glazes, where it is required in considerable proportion to prevent turbidity.

In alkaline glazes, including some lime glazes, one effect of alumina is to make the soluble silicates less soluble. In lead glazes, alumina increases the solubility and enables them to contain more silica, but an excess of it should be avoided as it causes turbidity.

When the ratio $\text{RO}:\text{R}_2\text{O}$ is not less than 1:1, alkaline and lime glazes can take up 0.5–0.6 molecular equivalents of alumina but no more. The $\text{RO}:\text{R}_2\text{O}$ ratio is very important when alumina is present.

In earthenware glazes, the molecular ratio of alumina to silica is best kept between 1:6 and 1:10, whereas in crystalline and matt glazes the molecular proportion of alumina should be much lower, e.g. 1:5.

In opaque glazes, alumina tends to reduce the amount of opacifier (tin or titanium oxide) required and to increase the temperature range.

Alumina tends to reduce crazing in fritted glazes and acts similarly to silica and boric acid together, though more powerfully than either of these two when used alone.

Keeler has observed the following effects of varying the ratio of alumina:silica in terra-cotta glazes:

Alumina:Silica Ratio	Product
High alumina, low silica	Immature glazes in most cases. If they do fuse, they tend to flaw and craze
Low alumina, low silica	Crazing, pinholes, immaturity
High alumina, high silica	Beading, immaturity, waviness, but no crazing
Low alumina, high silica	Fair bright glazes, with tendency to waviness

Alumina is used in the form of (i) china clay or ball clay, (ii) feldspar or Cornish stone. The two latter materials being fluxes, usually predominate, the clay being added, when required, to give the requisite adhesion to the ware. On account of its alumina content, clay is often effective in preventing crazing. Its chief value is that, being composed of very small particles, it combines more rapidly with some of the fluxes than the coarser forms of silicates. An excess must be avoided, as it makes glazes opaque, and insufficiently fusible.

Fluxes are employed in glazes to produce a material having the required fusing-point and transparency. The choice of the fluxes is very important.

It is desirable to have at least two bases in a glaze, and preferably three. Lead glazes are the only exceptions to this rule, for, owing to the peculiar behaviour of lead compounds with silica, one flux is sufficient, as it is easily possible to make

glazes of a mixture of lead oxide and silica without any other additions. Yet, even in lead glazes, it is often convenient to use a second base or flux. The fact that several fluxes produce a more fusible mixture than an equivalent proportion of one flux is due to the well-known law that one gram-molecule of a substance dissolved in any solvent causes a constant depression of the fusion-point, so that if several bases are present, each acts independently and the fusion-point is depressed to a correspondingly greater extent than that caused by an equivalent proportion of only one flux. In addition, a combination of fluxes increases the vitrification range and liquid formation progresses more smoothly.

In most leadless glazes, the fluxes are soda and potash, with the addition, in some cases, of lime, magnesia, baryta or zinc oxide.

Seger gives the following as the order of strength of various fluxes in glazes:

TABLE VI—XIX. FLUXING POWER OF GLAZE COMPONENTS

<i>Fluxes in Glazes (Order of Activity)</i>	<i>Fluxing Power of Colouring Oxides (Order of Activity)</i>
Lead oxide	Manganese oxide
Baryta	Cobalt oxide
Soda	Iron oxide
Potash	Uranium oxide
Zinc oxide	Chromium oxide
Lime	Nickel oxide
Magnesia	
Alumina	

Soluble bases should, as far as possible, be avoided, as they necessitate the fusion of the base with silica, known as *fritting*, which is both troublesome and costly, in order to produce an insoluble material. Soluble salts do not remain distributed uniformly through a glaze or engobe, but rise to the surface by capillary attraction and so are unable to react properly with the ingredients below the surface.

Potash is usually added in the form of felspar or Cornish stone, but potassium nitrate (nitre) and carbonate are sometimes used. Felspar adds the desired amount of flux in a more concentrated form than does Cornish stone, but if in excess it tends to cause peeling and may also cause crazing if the other constituents are not in the right proportions.

Both felspar and Cornish stone also add alumina and silica to a glaze, and this must, if necessary, be corrected by reducing the proportion of clay or flint used. Care should also be taken to ensure that the iron content is small, otherwise the glaze will be stained.

Soda is added in the form of a soda felspar or as a soluble salt, such as sodium carbonate, in which case *fritting* (p. 344) with some of the other constituents of the glaze is necessary. The action of soda is almost identical with potash and the two are often interchangeable. Sometimes soda produces a slightly more 'fusible' glaze and potash a rather more glossy one.

Glazes high in alkalies are generally suitable for bodies rich in quartz, whilst glazes low in alkalies are more suitable for bodies rich in alumina.

Lime is usually added as whiting or other form of a calcium carbonate, though calcium sulphate (plaster of Paris) is sometimes used. The addition of any lime compound increases the glossiness and fusibility of fine earthenware and stoneware glazes and slightly reduces the tendency to crazing. Lime glazes with no other base usually require 0.5 equivalents of boric oxide to give the required fusibility, but more than one equivalent tends to cause turbidity.

For the reasons stated on p. 346 it is better to use a mixture of soda (or potash) and lime in glazes than either of these substances separately. The usual permissible range of composition of these two substances (expressed as oxides) is

$$\left. \begin{array}{l} 0.6 \text{ K}_2\text{O} \\ 0.4 \text{ CaO} \end{array} \right\} \text{ to } \left\{ \begin{array}{l} 0.2 \text{ K}_2\text{O} \\ 0.8 \text{ CaO} \end{array} \right.$$

Soda may be partially or completely substituted for potash in the above molecular proportions. Lime glazes usually require at least four equivalents of silica and at least 0.5 equivalents of alumina to give a satisfactory gloss.

Magnesia can usually replace an equivalent of lime in a glaze. The chief effect is to make the molten glaze less viscous and so reduce the tendency to excessive 'running'. It sometimes produces a clearer glaze with brighter colours, but neither magnesia nor lime should be the sole base in a glaze.

Baryta (BaO), behaves similarly to lime in a glaze, but as barium has a much larger atomic weight than calcium, it tends to produce a more brilliant lustre.

Zinc oxide acts as a base and increases the fusibility of glazes. It also stabilises some colours and reduces the tendency to 'craze'.

Lead compounds are used in plumbiferous glazes and do not require any other flux, though others are often used to ensure greater stability. Insoluble lead compounds produce glazes which can be used at relatively low temperatures without requiring to be fritted. They give great mobility and a high refractivity to glazes, and consequently impart a great lustre and brilliance unobtainable by any other element, although barium compounds sometimes give similar results in leadless glazes containing soda and boric acid. Small variations in the composition of leadless glazes are important, and more likely to cause trouble than when lead is present. The lead compounds most frequently used are *white lead* ($2\text{PbCO}_3\text{Pb(OH)}_2$), *red lead*, Pb_3O_4 , and *litharge*, PbO , but *lead ortho-silicate* (2PbOSiO_2 , melting point 746°C.) and *lead meta-silicate* (PbOSiO_2 , melting point 765°C.) are also used. Soluble compounds, e.g. lead borate, are not permitted because of the risk of lead poisoning (see also p. 343).

Boric acid and **boric oxide** are used in some glazes in place of part of the silica to lower the fusing-point without materially altering the constitution of the glaze.

The dual behaviour of boric oxide—sometimes as an acid and sometimes as a base—appears to be closely related to the general composition of the glaze. Thus, Stull and Radcliffe found that when the base oxygen: acid oxygen ratio is less than 1:2, boric oxide behaves as an acid, whilst if the ratio is greater the boric oxide behaves as a base, but if the ratio is exactly 1:2, the boric oxide behaves as a free acid. When boric oxide behaves as an acid, it increases the tendency to crazing and when it behaves as a base it decreases the crazing.

TYPICAL GLAZES

THE following are typical formulae for glazes suitable for various purposes; they are by no means exhaustive, as the number of different compositions which can be used for each purpose is enormous:

Salt glaze is produced by throwing damp common salt into the kiln when its contents are at a sufficiently high temperature. The salt is decomposed by the heat and moisture, forming soda (Na_2O) and hydrochloric acid (HCl). The former combines with the silica and alumina, of which the articles are made, forming complex silicates, the composition of which appears to vary considerably. According to Barringer, the limits of the alumina:silica ratio in the ware within which it is commercially possible to produce a good salt glaze are 1:4.6 to 1:12.5, and Mackler—who analysed pieces of glaze carefully chipped from the ware—found that salt glazes vary in composition from

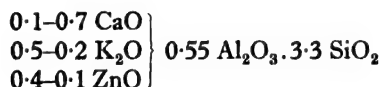


the average being

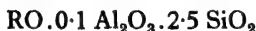


If an article is made of a highly aluminous clay deficient in free silica, it is usually very difficult to produce a good salt glaze on it, but the assumption that salt glazes are silicates and not aluminosilicates cannot be correct, as bricks made of pure silica do not form a good salt glaze when treated in the ordinary manner.

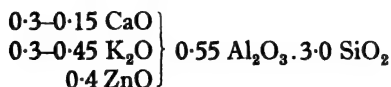
Terra-cotta glazes differ widely in composition, as the clays used in the manufacture of terra-cotta vary so greatly. A glaze which has long been used with success corresponds to the formula:



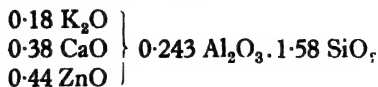
Stoneware consists of a vitrifiable body and can, therefore, be glazed at a higher temperature than most terra-cotta and faience ware. The composition of the glazes used, naturally varies with the clays of which the articles are made. Thus, Seger has stated that the best stoneware glazes correspond to the formula:



whilst R. Purdy considers that a typical formula is:



and a suitable Bristol stoneware glaze corresponds to:

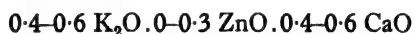


W. Scheffler has found that in transparent stoneware glazes for use under Cone 9, the silica should not exceed ten times the equivalent of the alumina or six times the actual weight of alumina and that at least 0.3 equivalents of potash should always be present, whatever the remaining 0.7 equivalents of bases may be.

Sanitary ware is largely made of fireclay covered with a felspathic engobe and a leadless glaze, which are fired at a temperature corresponding to Seger Cones 8 or 9 (1250° or 1280° C.). According to Parmelee and Williams,¹ the following requirements are important for fritted leadless glazes applied to sanitary ware:

- (a) The silica should be present to the extent of at least five equivalents.
- (b) The alumina should be 0.5–0.6 equivalents in the absence of boric acid, but may sometimes be less if 0.5 equivalents of boric acid are present.
- (c) The presence of 0.5 equivalents of boric acid is advantageous.

They found that a high proportion of lime caused dullness, a high proportion of zinc oxide caused blistering in the glaze, and a high proportion of alkali caused opalescence and crazing. In the best glazes they examined, the composition of the RO part of the glaze formula was:



An engobe and a glaze which may be regarded as the bases of most of those used in this country for sanitary ware—the variations being largely due to local circumstances—correspond to the formulae:

Engobe, $1.0 \text{ K}_2\text{O} . 22 \text{ Al}_2\text{O}_3 . 65 \text{ SiO}_2$

Glaze $\left\{ \begin{array}{l} 0.16 \text{ K}_2\text{O} \\ 0.64 \text{ CaO} \\ 0.20 \text{ ZnO} \end{array} \right\} 0.22 \text{ Al}_2\text{O}_3 . 2.5 \text{ SiO}_2$

It will be noted that this glaze does not conform to the conditions prescribed by Parmelee and Williams, yet it is extensively and satisfactorily used in this country, whilst glazes containing boric acid are seldom applied to sanitary ware.

Earthenware and Faience. Seger gives the following relations between the RO, silica, and alumina in various glazes:

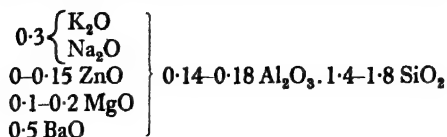
Glazes for common earthenware	{	1RO to 1.5 SiO ₂
and fine French faience		1RO to 3 SiO ₂
Glazes for English and German	{	1RO . 0.01 Al ₂ O ₃ . 2.5 SiO ₂
white earthenware		1RO . 0.4 Al ₂ O ₃ . 4.5 SiO ₂

As stated on p. 346, the proportions of the various RO oxides are important. Earthenware glazes with 0.7 Na₂O and 0.3 CaO tend to craze, but by transposing these two proportions, good white glazes and at higher temperatures a good stoneware glaze can be obtained.

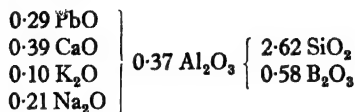
According to E. Berdel² earthenware glazes free from lead and boric acid for temperatures between Cones 1 and 6 should have compositions within the following limits:

¹ Parmelee, C. W. and Williams, E., *Trans. Amer. Ceram. Soc.*, 18, 812 1916.

² Berdel, E., *Ker. Rund.*, 25, 88, 1917.

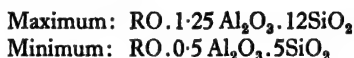


A typical glaze for English earthenware (tableware) corresponds to:

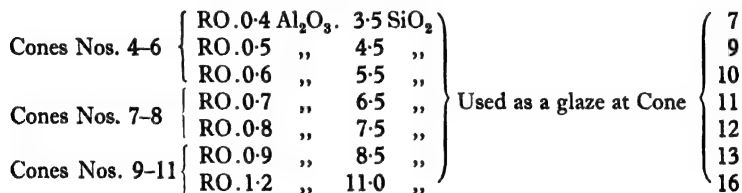


As the terms 'earthenware' and 'faience' include many kinds of ware, from those made of crude red-burning clay covered with a roughly-made glaze composed of galena and crushed quartz, flint, or fine sand, to some of the finest examples of the potter's art, no single formula can possibly prescribe the limits of composition of glazes and engobes for such a variety of wares.

Porcelains, like earthenware, vary greatly in composition and the glazes vary correspondingly. Seger has stated that the following are the maximum and minimum compositions for hard porcelain glazes:



but he recommended that such glazes should be based on the composition of some Seger cones, and Mellor¹ has suggested that the compositions shown below (which approximate to Cones 4-11) may be used as glazes for feldspathic porcelain.



Opaque² and opalescent glazes are made of the same materials as clear glazes with the addition of one or more opacifying agents. The opacity may be produced:

(a) By adding a substance, such as tin oxide, which remains suspended in the glaze and renders it opaque and white.

(b) By adding a substance, such as alumina, which can dissolve in the molten glaze but crystallise out on cooling and so produce opacity. Titanium oxide, zirconia and alumina are of this kind.

(c) By so composing the glaze that two immiscible products are formed in the kiln, one being uniformly distributed through the other, so that on cooling an opaque

¹ Mellor, J. W., *Trans. Eng. Ceram. Soc.*, 14, 176, 1914.

² For further information on opacity as a property of some ceramic materials, see Chapter XIV.

glaze is formed. Calcium borate, calcium phosphate and calcium fluoride are used in this manner.

The maximum opacity is obtained with particles of about 0.25×10^{-3} mm. Such particles are much too small to be produced by grinding but are readily obtained when sufficient of the opacifier is dissolved in a molten glaze and the latter is then allowed to cool slowly.

Glazes rich in alkali or lead tend to dissolve an excess of the opacifier and produce irregular results. Fluorides, on the contrary, increase the fluidity of the molten glaze and also its opacity.

The opacifiers chiefly used in ceramics are:

(a) *Tin oxide*—usually in the form of *tin ash*—made by calcining a mixture of 60–80 parts of granulated lead with 40–20 parts of granulated tin, with frequent stirring. About 8–10 per cent of the tin oxide is usually sufficient; 5 per cent is sometimes ample. Some glazes have too solvent an action on tin oxide and make its use impracticable. This opacifier is unsuitable for highly alkaline glazes.

(b) *Titanium oxide* (anatase, rutile or the specially prepared oxide).

(c) *Zirconia or Zircon or sodium zirconate or sodium zirconium silicate*.¹

(d) *Antimony oxide*.

(e) *Arsenic oxide*.

(f) *Calcium fluoride*.

(g) *Cryolite*.

(h) *Tricalcium phosphate* (bone ash) and *calcium pyrophosphate, magnesium phosphate, zinc phosphate and lead phosphate* are all suitable in alkaline glazes but less satisfactory in lead glazes.

Matt glazes are chiefly made from transparent glaze mixtures by:

- (i) Reducing the proportions of base or flux.
- (ii) Adding zinc oxide, magnesia or alumina (or china clay).
- (iii) Reducing the finishing temperature or the duration of the heating at or near that temperature.

The change which occurs is usually due to the saturation of a clear glaze with a substance which fuses at the oven temperature but is precipitated or crystallises when the glaze is cooled slowly.

Great skill is needed in order to obtain a pleasing effect as small errors in the composition of the glaze or the use of a substance in too coarse a powder may have a disastrous effect.

C. F. Binns² considers that matt glazes fired at a temperature corresponding to Cone 01 are best produced by using a mixture corresponding to



He has suggested that the best composition for the RO bases is 0.09 K₂O, 0.20 CaO, 0.575 PbO, 0.135 ZnO, but the following may also be used:

¹ About 7–10 per cent of alumina should also be present to restrict the solubility of the zirconia; a little lime will increase the opacity.

² Binns, C. F., *Trans. Amer. Ceram. Soc.*, 5, 50, 1903 and 7, 115, 1905.

TABLE VI—XX. COMPOSITION OF RO BASES IN MATT GLAZES

<i>a</i>	<i>b</i>	<i>c</i>
0.225 K ₂ O	0.135 K ₂ O	0.200 CaO
0.575 PbO	0.170 CaO	0.575 PbO
0.200 ZnO	0.575 PbO	0.225 ZnO
	0.120 ZnO	

Some matt glazes when heated excessively, or when cooled too quickly, produce glossy glazes.

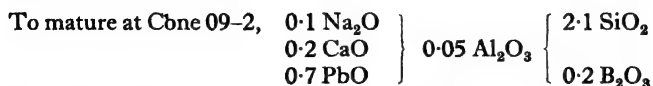
Crystalline glazes are most satisfactorily produced from glazes which are free from alumina, as this substance tends to prevent crystallisation, but if only 0.15 equivalent of alumina is present it may not interfere. Lime or zinc oxide appears to be essential for the production of good crystals. The chief oxides which give good crystals and may be regarded as crystallising agents are: zinc oxide, titanium oxide, tungstic oxide, molybdic oxide, vanadic oxide, and bismuth oxide. Oxides of manganese, uranium, cobalt, iron, copper, and nickel may also be used for coloured glazes. According to Koerner¹ bismuth oxide and uranium oxide produce crystalline glazes at as low a temperature as Cone 010–09, and tungstic oxide produces beautiful fernlike and star-shaped formations, showing partly iridescent reflexes quite unlike the effects obtained with zinc and titanium oxides.

Purdy and Krehbiel² found that manganese dioxide had the greatest tendency to cause crystallisation; zinc oxide is next, but with it the crystals tend to segregate in local areas, leaving others devoid of crystals. If a fusible silicate (glaze) is coloured (as by adding cobalt) and is then saturated with zinc silicate whilst in the molten state, the zinc silicate will crystallise out as willemite and will be stained blue, the background remaining colourless if there is no excess of colouring agent.

Titanic oxide produces very small crystals uniformly distributed through the glaze.

Although glazes with a 1:4 oxygen ratio are commonly used in the production of crystalline glazes, Purdy and Krehbiel consider an oxygen ratio of 1:2.8 to produce better and more uniform crystalline glazes. The lower oxygen ratio is confirmed by the researches of Schott on Jena glass.

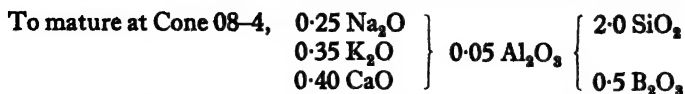
The composition of the 'foundation glaze' from which crystalline glazes may be prepared by suitable additions is very important; the following are typical formulae for this kind of glaze:



To this is added 18–28 per cent of a crystallising agent.

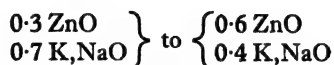
¹ Koerner, J., *Trans. Amer. Ceram. Soc.*, 10, 61, 1908.

² Purdy and Krehbiel, *Trans. Amer. Ceram. Soc.*, 9, 319, 1907

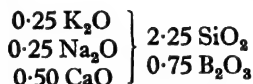


To this is added 2-25 per cent of rutile or 0.25-2 per cent of oxides of chromium, cobalt, or copper, or 5-10 per cent of the oxides of iron, manganese, uranium or nickel.

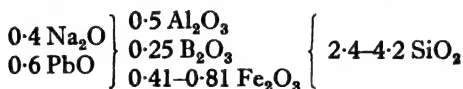
Purdy and Krehbiel have suggested that the best proportions of zinc to alkali are:



Aventurine Glazes. The presence of finely-divided metallic particles in a glaze produces a spangled effect, resembling the mineral aventurine. Mackler¹ has used a glaze corresponding to:



together with 20 per cent of finely-divided metallic iron, and H. G. Schurecht² has found that red to black aventurine glazes may be produced with 0.41-0.81 equivalents of iron oxide in a glaze of the following composition:



Glazes with 0.41-0.73 Fe_2O_3 give a red colour under oxidising conditions and a black one under reducing conditions. The ratio of iron oxide to silica is important, glazes containing 2.4 SiO_2 requiring at least 0.41 Fe_2O_3 , and glazes containing 4.2 SiO_2 requiring at least 0.58 Fe_2O_3 . Greater amounts of iron oxide increased (a) the size of the crystals, (b) the number of crystals, (c) the refractoriness of the glaze.

Other metals, particularly copper and gold, may be used instead of iron. It is not necessary to employ the metals, as, if the conditions of firing are suitable so that compounds are reduced to the metallic state, an aventurine effect will be produced. If the particles of metal are too small they will dissolve in the glaze and will merely colour it, producing a 'stained glaze'.

THE COLOURING OF GLAZES

THE colouring of glazes and glazed bodies is a science in itself and has occupied the attention of ceramists from the earliest days of glazed-ware manufacture.

Glaze ware is usually coloured in one of three ways:

(a) *Under-glaze decoration*—where the colours are applied to the ware after it has been 'bisque' fired. The colours are usually applied in the form of a spray or as a paste and are finely-ground mixtures of metallic compounds with china clay and

¹ Mackler, E., *Tonind. Zeit.*, 207, 1890.

² Schurecht, H. G., *J. Amer. Ceram. Soc.*, 3, 971, 1920.

felspar. Some underglaze colours which have an oil base have to be hardened at about 600° C.; the ware is then covered with a transparent glaze.

Underglaze decoration has the advantage of being completely protected from abrasion and so it is permanent. It is, however, flat and dull in appearance and the range of colour and design is limited because of the risk of attack by the glaze during its maturing.

(b) *On-glaze decoration*—where the colours are applied on top of the glaze. In this form of decoration the ware is refired to harden the colours at a temperature which is insufficient to soften the glaze. Consequently, on-glaze colours are compounded from low-melting components—usually frits—with a coloured metallic compound.

Because on-glaze decoration is a surface application, it is not as resistant to chemicals and abrasion as is under-glazed ware, but the colours are more brilliant and lustrous and because the temperature at which the on-glaze is fired is low (750–850° C.) a greater variety of colours are available.

On-glaze decoration is usually applied to ware which has been covered with an opaque glaze or to a white body with a transparent glaze.

(c) *Coloured or majolica glazes*.—Metallic compounds are frequently added to glazes which are then applied to ware to give an overall coloured covering.

Such glazes are similar in composition to normal transparent glazes—apart from the addition to produce the colour—and a complete range with different softening temperatures is available.

Colouring Compounds. The ingredients which are used to produce a particular colour for glazed ware are mostly closely-guarded secrets of the manufacturer. Although certain metallic compounds are known to produce a colour, the shade or tint can often be influenced by additives or by the type of flux which is used.

Most of the compounds which are used for glaze coloration are salts of metals of the transitional groups or those with relatively unstable outermost orbits of electrons (see Chapter II). By a mechanism of electron transfer within the orbits of their atoms, such elements preferentially absorb light of certain wavelengths, thereby appearing coloured.

The elements used to produce colours in ceramic glazes are many, but the most common have been summarised by Henry¹ and are as follows:

Yellow and Orange

1. A mixture of *lead oxide* and *antimony oxide* with small amounts of zinc oxide, tin oxide, calcium carbonate, aluminium oxide and iron oxide produces varying shades of yellow from lemon to orange depending on the proportion of the ingredients which are used. This is an excellent colour combination provided the temperature of firing is not too high. It is called *Naples yellow*.

2. *Cadmium sulphide* also produces a bright yellow and is suitable for overglaze decoration but will not withstand a high temperature.

3. Mixed oxides or other salts of *titanium*, *antimony* and *chromium*. This gives a stable colour at most temperatures and under most glaze conditions.

4. A mixture of *tin oxide* and *vanadium pentoxide* with small amounts of

¹ Henry, P., *Bull. Amer. Ceram. Soc.*, 36, 431, 1957.

alumina and titania produces a very stable yellow, suitable for majolica and terracotta glazes. It is extensively used to produce yellow sanitary ware or tiles.

5. A combination of *zirconia* and *vanadium pentoxide* gives a similar colour to the above. Although it is a cheaper product it is not so stable.

6. *Uranium salts* give yellow colorations, but are not widely used.

Red

Red coloration in glazes is produced almost exclusively from a combination of *cadmium sulphide* and *selenium*. The higher the proportion of the latter ingredient, the deeper is the shade.

Pink

Gold produces the most beautiful shades of pink, especially when used with titanium frits. *Chromium salts* combined with *tin oxide* or *alumina* will also produce pinks but these mixtures must be chosen carefully as they are not stable in all glaze compositions.

Blue

Cobalt oxide is used almost exclusively as a source of blue coloration. The shade may be modified by different additions; with silica a purplish blue is given, whilst with a combination of zinc oxide and alumina a greenish blue is developed.

Green

1. *Copper salts* form beautiful green or bluey-green colorations which unfortunately are not very stable and are particularly prone to vary with different kiln atmospheres. In an alkaline glaze, copper gives a transparent turquoise coloration, but under acidic conditions it is green.

2. *Chromium oxide* is the principal agent for producing green colorations. It is very stable under most conditions.

Black

1. A mixture of the *oxides* or *salts* of *cobalt*, *chromium*, *iron* and *manganese* gives a stable neutral black and is of common use in glaze ware.

2. The above components, without chromium salts, give a characteristic metallic bluish black.

3. *Chromium oxide* with *copper oxide* gives a black colour which is stable only at low temperatures.

4. The *oxides* of *chromium*, *iron* and *manganese* produce a brown-black which is stable to high temperatures.

Brown

Iron oxide, *chromium oxide* and *zinc oxide* form the basis of most brown colours for glazes. Manganese dioxide when added to the mixture gives a dark brown whilst alumina produces a lighter, yellow brown.

White

Tin oxide is the component most commonly used to give a white glaze. To produce the purest shades all the ingredients of a glaze must be chosen carefully because a minute proportion of iron oxide gives a yellow tint. A small amount of cobalt oxide is occasionally added to mask the yellowing effect of iron oxide.

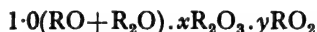
The colour of a body or glaze is dependent on factors other than the type of colouring oxide which is added. These include:

- (a) The amount of colouring agent added.
- (b) Its reaction with the other components of the body or glaze. Iron compounds, for example, normally burn red, but if appreciable lime is present, the colour of the fired body is white, cream, buff or brown, depending on the relative proportions of the iron and lime.
- (c) The temperature and duration of the firing.
- (d) The atmosphere in the kiln during burning. A reducing atmosphere gives rise to brown, grey and blue colorations in ware containing iron which otherwise would burn red.
- (e) The particle size and state of combination of the colouring agent. Both these factors influence the rate of reaction with the body.

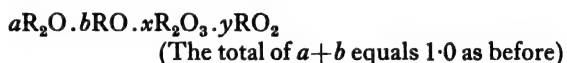
Several manufacturers specialise in the production of colours for most types of ware and they offer a wide range to the intending user.

COMPOUNDING CERAMIC GLAZES

ALTHOUGH complex mixtures are often used for ceramic bodies and glazes their effective composition can be greatly simplified by regarding them (especially after they have been fired) as mixtures of simple oxides, corresponding to a general formula



It is better to divide the bases into two groups and to write the formula as



The division of the bases enables the ratio of the R_2O and RO groups to be clearly shown, and sometimes this ratio is very important (p. 347).

The chief oxides may then be arranged as follows:

R_2O	RO	R_2O_3	RO_2
Na_2O	CaO	Al_2O_3	SiO_2
K_2O	MgO	B_2O_3	TiO_2
Li_2O	ZnO		ZrO_2
	PbO		

Ceramic materials cannot have strict chemical compositions which correspond to chemical formulae as they are subject to too many influences on firing. It is, however, very convenient to make use of chemical formulae as guides even though they do not wholly represent the facts.

It is customary to ignore elements present in very small proportions, but care must be taken, as they sometimes have important effects. Another important precaution is to use accurate chemical analyses of the materials actually used and not 'general figures', or serious errors may occur.

Calculation of Molecular Formulae. A chemical analysis of a ceramic body indicates the composition in terms of oxides calculated on a *weight percentage* basis. To convert this to a *molecular* basis, the values have to be divided by the molecular weight of the corresponding oxide, which is found by adding together the atomic weights (see Chapter II, Table 1B) of the components; it is sufficiently accurate to calculate to the first place of decimals.

The molecular weight of alumina, Al_2O_3 (atomic weights—Al = 27.0; O = 16.0) is

$$2 \times 27.0 + 3 \times 16.0 = 102.0$$

Similarly silica (SiO_2), is

$$1 \times 28.1 + 2 \times 16.0 = 60.1$$

and water (H_2O), is

$$2 \times 1.0 + 1 \times 16.0 = 18.0$$

Example: The ideal chemical composition of kaolinite is $\text{Al}_2\text{O}_3 = 39.50$ per cent; $\text{SiO}_2 = 46.56$ per cent; $\text{H}_2\text{O} = 13.94$ per cent. The molecular composition is:

$$\text{Al}_2\text{O}_3 = 39.50 \div 102.0 = 0.387;$$

$$\text{SiO}_2 = 46.56 \div 60.1 = 0.774;$$

$$\text{H}_2\text{O} = 13.94 \div 18.0 = 0.774;$$

i.e. 0.387 Al_2O_3 ; 0.774 SiO_2 ; 0.774 H_2O .

For convenience the fractions are eliminated by dividing throughout by 0.387, giving;



The total molecular weight of kaolinite is:

$$102.0 + 2 \times 60.1 + 2 \times 18.0 = 258.2$$

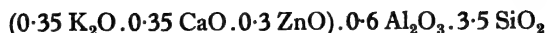
The molecular composition of orthoclase feldspar and muscovite mica can be calculated similarly from the data in Table VI.XI (p. 322).

Some useful molecular weights are given in Table VI.XXI.

When calculating the composition of a body or when compounding a glaze, the molecular composition of the actual ingredients used must be determined, paying attention to minor components as well as those of major importance, and taking into account any constituents which may be volatile on heating.

The body or glaze to be compounded must also be calculated in terms of the molecular proportions of its oxides, and its components attributed to those in the ingredients to be used. This is best demonstrated by considering an example.

Example: to compound a Bristol glaze of composition



from feldspar ($\text{K}_2\text{O} . \text{Al}_2\text{O}_3 . 6\text{SiO}_2$), china clay ($\text{Al}_2\text{O}_3 . 2\text{SiO}_2 . 2\text{H}_2\text{O}$), flint (SiO_2), whiting (CaCO_3) and zinc oxide (ZnO). (For convenience, the ideal compositions of the components have been taken, but in practice they must be determined.)

The CaO and ZnO in the glaze come from the whiting and zinc oxide respectively. The K_2O content comes from the felspar but this ingredient also contributes

TABLE VI—XXI. MOLECULAR WEIGHT OF IMPORTANT COMPONENTS OF CERAMIC BODIES

Oxide	Molecular Weight	Compound	Molecular Weight
SiO ₂	60.1	Flint, quartz SiO ₂	60.1
Al ₂ O ₃	102.0	Kaolinite Al ₂ O ₃ .2SiO ₂ .2H ₂ O	258.2
TiO ₂	79.9	Orthoclase felspar K ₂ O.Al ₂ O ₃ .6SiO ₂	556.8
Fe ₂ O ₃	159.8	Albite felspar Na ₂ O.Al ₂ O ₃ .6SiO ₂	524.6
FeO	71.9	Anorthite felspar CaO.Al ₂ O ₃ .2SiO ₂	278.3
CaO	56.1	Muscovite mica K ₂ O.3Al ₂ O ₃ .6SiO ₂ .2H ₂ O	796.8
MgO	40.3	Mullite 3Al ₂ O ₃ .2SiO ₂	426.2
K ₂ O	94.2	Whiting CaCO ₃	100.1
Na ₂ O	62.0	Cornish stone (average)	770.1
B ₂ O ₃	69.6	0.4 Na ₂ O 0.5 K ₂ O 0.1 CaO } 1.25 Al ₂ O ₃ .9.25 SiO ₂ 0.8 H ₂ O	
PbO	223.2		
ZnO	81.4		
H ₂ O	18.0		
CO ₂	44.0		

some alumina and silica. The remainder of the alumina comes from the clay and any excess silica required will be provided by the flint:

The proportions of each ingredient may then be calculated as in Table VI.XXII.

GLASSES

TO some extent, a glass may be likened to an overvitrified glaze, and indeed many of the general rules applicable to glazes, hold also for glasses.

A glass is a true super-cooled liquid and although it appears hard and solid at room temperature, it has all the properties of a highly viscous liquid; it will flow if a load is applied to it and, on heating, it becomes progressively more fluid, finally becoming free-flowing.

Glasses differ from glazes in having a higher proportion of flux, i.e. a greater amount of alkali and alkaline earth elements. This is mainly so that melting will take place at a lower temperature—in fact, the initial softening point of many glasses is about 600° C.

TABLE VI—XXII. THE COMPOSITION OF A GLAZE

Glaze composition		CaO	ZnO	K ₂ O	Al ₂ O ₃	SiO ₂	H ₂ O	CO ₂	Weight required Prop. × molecular weight	Weight Proportion per cent
Components	Molecu- lar weight	Molecu- lar Prop.								
	Whiting (CaCO ₃)	100.1	0.35	—	—	—	—	0.35	0.35 × 100.1 = 35.035	
	Zinc oxide (ZnO)	81.4	0.30	—	—	—	—	—	0.30 × 84.1 = 24.230	
	Felspar (K ₂ O, Al ₂ O ₃ , 6SiO ₂)	556.8	0.35	—	0.35	2.10	—	—	0.30 × 556.8 = 167.040	
	Kaolinite (Al ₂ O ₃ , 2SiO ₂ , 2H ₂ O)	258.2	0.25	—	0.25	0.50	0.50	—	0.25 × 258.2 = 64.550	
	Flint (SiO ₂)	60.1	0.90	—	—	0.90	—	—	0.90 × 60.1 = 54.090	
Total		0.35	0.30	0.35	0.60	3.50	0.50	0.35	344.945	100.0
								volatile		

The proportions required to compound the glaze of formula 0.35 CaO, 0.30 ZnO, 0.35 K₂O, 0.60 Al₂O₃, 3.50 SiO₂ are 10.2 parts of whiting, 7.0 parts of zinc oxide, 48.4 parts of felspar, 18.7 parts of kaolinite and 15.7 parts of flint.

The principal components of glasses are (1) soda, potash, lime, magnesia and baria as bases, of which soda and lime are the most common; (2) silica and boric oxide, which may be considered as acid components, although the latter can have dual behaviour; (3) alumina, which helps to prevent crystallisation on cooling and has other desirable effects; (4) other ingredients added to impart colour, appearance, resistance to chemical attack, low expansion characteristics, high melting point, hardness, etc. These include iron oxide, manganese dioxide, lead oxide and zinc oxide.

The main ingredients used in the manufacture of glasses are similar to those used in compounding ceramic bodies and glazes. Silica sand is the principal source of silica, felspar of alkali and alumina, limestone of calcium oxide, borax of boric oxide. Quantities of soda ash (crude sodium carbonate), sodium sulphate and sodium nitrate are also incorporated to provide a high content of alkali. Of major importance in glass-making, is that the ingredients should be free from iron contamination, because even small quantities of this impurity cause serious discoloration of the product (see p. 314).

The chief effects of the principal oxide components in glasses are as follows:

1. *Silica* is the major acidic oxide and combines with the basic components. Large proportions of silica increase the melting and softening point of glasses and also lower the thermal expansion.

2. *Boric oxide* can replace silica to some extent in glasses and has the advantage of lowering the melting point, so that by a suitable combination of silica and boric oxide, a glass of low expansion, but with a reasonable working temperature can be manufactured.

3. *Alumina* reduces the melting point, prevents crystallisation when present in certain proportions, and reduces the solubility of many glasses in water and other chemicals.

4. *Sodium and potassium oxides* are the principal fluxes in glasses, and with silica form a low melting-point liquid. Such glasses have a high thermal expansion.

5. *Lime* is another major source of flux, but it does not form a liquid phase with silica as readily as does sodium. However, when it replaces sodium, the glass has an appreciably lower thermal expansion.

6. *Magnesia* is used as a replacement for lime but the liquids which it produces are more viscous, although they crystallise less readily.

7. *Baria* behaves rather like magnesia, but also imparts a high lustre to the glass. *Lead oxide* behaves similarly.

As in glazes, it is advisable to have at least two fluxing oxides in glasses, to produce a more satisfactory melt with a longer working range.

Although a consideration of the role of the various oxide components of glasses and glazes in terms of their chemical activity is convenient and simple, it provides only a first indication of their behaviour. Each element present plays an integral and important part in determining the structure of the glass, which has been described in Chapter III (p. 170). The cations and anions in glasses are randomly arranged, so that the structure of such materials differs from that of an ordered crystal. The number of chemical materials which can form glass network structures is limited and *silica* (SiO_2) and *boric oxide* (B_2O_3) are the principal sources in commercial glasses.

Other elements, e.g. *aluminium*, *magnesium* and *lead* can partially replace silicon or boron in the structure and so confer valuable properties, but the amounts which can be incorporated are limited and an excess of them will cause crystallisation. Elements of large ionic size and small charge occupy holes in the crystal lattice of the glass and appear to act as nuclei around which the glass structure forms. These elements, which include *sodium*, *potassium*, *calcium* and several others, determine many of the important characteristics of glasses which contain them. The amount of such interstitial ions which can be contained depends principally on the net residual negative charge in the network structure. A silica lattice is theoretically electrically balanced, but, in practice, some defects are always present so that a small proportion of alkali ions can be contained. When aluminium replaces silicon, charge deficiencies are introduced, so that more alkali ions can enter the structure to produce a balanced lattice. The limits to which such a process can be carried, are governed by the amount of lattice replacement which can be accommodated without crystallisation.

The compositions of several types of glasses are given in Table VI.XXIII.

TABLE VI—XXIII. THE COMPOSITIONS OF SOME GLASSES

Constituent	Window	Flint	Crown	Bottle	Pyrex	Electric lamps and valves
SiO ₂	72.0–72.5	45.0–70.0	58.0–74.0	72.0–74.0	80.4	48.8
Al ₂ O ₃	0.5–1.7	0.0–2.0	—	1.0–3.0	2.2	17.7
Fe ₂ O ₃	—	—	—	0.0–2.0	—	—
CaO	10.0–8.0	0.1–0.4	0.0–2.5	3.0–5.0	0.4	12.4
MgO	4.0–3.2	—	—	0.0–4.0	0.1	—
Na ₂ O	13.5–16.0	1.0–16.0	3.0–5.0	12.5–17.0	4.0	—
K ₂ O	—	7.0–0.0	9.0–15.0	—	0.6	—
Li ₂ O	—	—	—	—	—	6.7
B ₂ O ₃	—	—	3.0–7.0	—	12.3	—
PbO	—	48.0–10.0	—	—	—	—
BaO	—	—	20.0–0.0	—	—	—
ZnO	—	0.0–4.0	5.0–0.0	—	—	—

CEMENTS, MORTARS AND OTHER BONDING AGENTS

A CEMENT or bonding agent is used to impart strength to a material which otherwise would be too weak mechanically for the purpose for which it is intended. Many substances can be considered as cements and they can be divided into two general classes:

1. Amorphous materials which form a continuous film around the non-cementing material and so hold it together, and
2. Crystalline cements, which form a felted mass of interlocking and inter-growing crystals.

AMORPHOUS CEMENTS

AMORPHOUS CEMENTS include gums, resins and glasses. The mechanism by which such materials act as adhesives is not known with certainty. It is believed by some authorities that they form a continuous phase of high viscosity throughout the mass and completely enclose the other materials which may be present. Water can behave

similarly, because some non-plastic bodies, e.g. sand, form a stronger mass when green (i.e. wet) than when dry. Surface tension effects may play a predominant part in their bonding action. Many examples of amorphous cements are known in ceramic practice.

(a) **Organic Binders.** Various gums, of which *cellulose sulphite lye* is the most common, are frequently added to non-plastic materials so that they can be moulded into shapes which have a reasonable strength on being dried. Other materials used include linseed oil, fat, gelatin, dextrin, various gums, rubber latex, resins, starch, tar and pitch.

All these substances decompose at a comparatively low temperature, so that their cementing action is destroyed. For many purposes, this is not a serious disadvantage, because the strength which they confer is required only to allow the ware to be handled and used at ordinary temperatures. The loss of strength on low temperature firing in bricks of non-plastic material is disadvantageous, however, in that it limits the numbers which can be stacked together in the kiln or furnace.

(b) **Inorganic binders**—some substances form gels which behave as gums or resins in forming a continuous film in a compacted body, but which are not destroyed by heat. *Colloidal gels* of many inorganic substances can behave in this way and perhaps the best example is colloidal silica which is a natural cementing agent in quartzites, ganisters and some fireclays; colloidal iron and alumina can behave similarly. As early as 1912, a process for bonding magnesia bricks with colloidal magnesium hydroxide was patented.

The principal difficulty with this type of bond is to obtain the correct incorporation of the non-plastic aggregate with the cementing agent, and the most suitable method is to precipitate the gel in contact with the particles of the body. A solution of sodium silicate forms silica gel when acid is added to it and this is a common form of cement used in ceramic practice. Sodium silicate itself forms very viscous solutions, is a very effective bond and is the basis of most acid-resisting cements.

The drawback of cementing material containing alkalis is that they reduce the refractoriness of bodies which contain them. The use of an *organic silicate* compound has largely obviated this difficulty and commercially-manufactured *ethyl silicate* or one of the proprietary *silicones* are being increasingly applied. These materials are supplied as liquids which decompose upon hydrolysis or at a comparatively low temperature to give amorphous silica of great purity. Not only do such materials impart strength to a compacted powder but their reactions at high temperature with other ingredients can be put to advantage. Williams¹ has described how a high-grade mullite refractory may be synthesised by bonding alumina with ethyl silicate and firing to a temperature at which reaction occurs. Similarly zircon (zirconium silicate) can be synthesised from zirconia and the organic silicate.

CRYSTALLINE CEMENTS

Of greater effectiveness and permanence, are the materials which react (usually with water) to form a felted mass of needle-shaped crystals which has great tenacity. The setting properties of *calcined lime* were well-known to the Romans and this material is

¹ Williams, A. E., *Refract. Journ.*, 28, 453, 1952.

still in common use. Calcined limestone—heated at about 900°C . to form the oxide—is mixed with sand in the proportions of about 1:3. In the presence of water, hydrated calcium silicates are formed and also some calcium hydroxide and water. *Lime mortars*, as they are termed, set slowly and are not very strong, but they are cheap to manufacture and easy to use, so they were commonly employed until recent years as cementing materials for brick structures. Excess lime was invariably present and undoubtedly many severe cases of efflorescence could be attributed to this source.

Many calcium compounds have remarkable cementing properties.

Plaster of Paris, $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$, is an ideal material for making ceramic moulds. It is made into a slip with water and poured into a suitable former and on standing crystallises as gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, which forms a strong mass of interlocking needles. Such bodies are porous and they ‘filter’ clay and other slips which are poured into them. The manufacture of Plaster of Paris has been described on p. 329.

The most widely-employed cements, however, are *calcium alumino-silicates* which set to a hard, strong mass with water. These include Portland and high-alumina cements; the former are the active ingredients in concrete and other structural materials and the latter are commonly used in refractory cements and *castable* ceramic bodies.

Portland cement is usually manufactured by heating limestone and clay to about 1600°C . in a rotary kiln. The cycle of reactions is highly complex and the nature of the final product is not fully understood, but it contains lime, alumina, silica, magnesia and iron oxides as components. The predominant compound is tri-calcium silicate ($3\text{CaO} \cdot \text{SiO}_2$), but dicalcium silicate ($2\text{CaO} \cdot \text{SiO}_2$), tetra-calcium aluminium ferrite ($4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$), tricalcium aluminate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3$) and alite (see Chapter III, p. 114) are also present. Small amounts of impurity may have an important influence on the setting properties. Portland cement is the cementing agent in *concretes* where it is mixed with an aggregate of stone or pebbles in the ratio of about 1:6. Water is essential to the setting process, which involves the hydration of the calcium compounds. Portland cement is not suitable for use above about 250°C . and is not very resistant to solutions containing acids. Its composition is shown in Table VI.XXIV.

Aluminous cements contain calcium aluminates as their active components which hydrate when mixed with water. The manufacturing methods of these types of cement are still largely trade secrets but the principal ingredients are limestone and alumina with other minor additives to promote the most suitable product. The temperature of calcination in the rotary kiln is usually much higher than that used in the manufacture of Portland cement; in fact, the materials are heated almost to their fusion point.

The range and scope of aluminous cements are very great. They are of advantage because they set rapidly, are resistant to sea water and withstand greater temperatures than Portland cement.

The aluminous cements can be divided into two general classes depending on the amount of alumina which they contain.

(1) **38–40 per cent** alumina by weight comprises the range of cements known as *ciment fondu*. The active compound in such cements is mono-calcium aluminate

($\text{CaO} \cdot \text{Al}_2\text{O}_3$), but other ingredients, particularly iron oxide, are present in large amounts and are essential to the economical preparation of the cement. The melting point of pure monocalcium aluminate is about 1600°C ., but, in the commercial materials, an upper limit of 1300°C . should never be exceeded. Ciment fondu is widely used as the active constituent in refractory concretes. It is incorporated with a suitable 'grog', mixed with water, shaped and allowed to set, which it does in a matter of a few hours. One of its chief uses is in the manufacture of fireplaces and their surrounds, when it is mixed with sand or fireclay grog. Robson¹ has described the Continental practice of making brick kilns of ciment fondu and a crushed refractory aggregate usually of well-burned chamotte. Such material will withstand temperatures of up to 1350°C ., provided that the refractory aggregate contains over 40 per cent alumina. If the refractoriness of the aggregate is increased by using crushed sillimanite or corundum, the maximum temperature at which the concrete can be used is correspondingly increased. Ciment fondu is also valuable in the manufacture of light-weight refractory concretes, using crushed insulating bricks, vermiculite, diatomite, or bloated clay as aggregate.

Vast monolithic units of concrete can be cast and these have obvious advantages over the conventional brick-work structures.

Robson² has also indicated the value of ciment fondu in the ceramic and brick industries and in the manufacture of refractory concrete for gas-works and coke-oven plant. He recommends that a fireclay grog be used as aggregate and suggests the following mixtures to meet all purposes.

	Mix A	Mix B	Mix C
Coarse aggregate ($\frac{3}{4}$ – $\frac{1}{8}$ in.)	3 cu. ft.	2 cu. ft.	—
Fine aggregate ($\frac{1}{8}$ in. to dust)	2 cu. ft.	2 cu. ft.	$2\frac{1}{2}$ cu. ft.
Alumina cement	1 cu. ft.	1 cu. ft.	1 cu. ft.

(2) **60-75 per cent alumina cements** are of comparatively recent development and although they are of high cost, they are of great potential value in refractory concretes and the so-called *refractory castables*. The active ingredient of such cements is tricalcium penta-aluminate ($3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$)³ which has a melting point in excess of 1700°C ., and, because the impurity content can be kept low, commercial cements of this type, when admixed with a suitable grog, can withstand temperatures up to 1700°C . Many alumina cements (with up to 75 per cent alumina) have been manufactured and 'Secar 250' is a common type used in Europe and is of wide application in North America. According to Robson,⁴ it has a setting time of 3–4 hours, and so rapidly does it develop strength that castable mixes made from it can be used within 24 hours. The strength of mixtures is between 2,500–3,500 lb. per sq. in. depending on the proportion of cement and this strength is maintained to high temperatures even under heavy loads.

¹ Robson, T. D., *The British Clayworker*, 62, 302, 1954.

² Robson, T. D., *Claycraft*, 28, 244, 1955; *Coke and Gas*, 1952, p. 241.

³ Dr. E. Hammond, in a private communication, has indicated that the principal mineral in Secar 250 is calcium di-aluminate ($\text{CaO} \cdot 2\text{Al}_2\text{O}_3$) and that the mineral $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$ does not exist.

⁴ Robson, T. D., *Refract. J.*, 203, 1954.

The chemical compositions of some calcium aluminosilicate cements are shown in Table VI.XXIV.

TABLE VI—XXIV. CHEMICAL COMPOSITION OF SOME CEMENTS

	<i>Portland</i>	<i>Ciment Fondu</i>	<i>High-alumina</i>
	per cent	per cent	per cent
CaO	60-66	35-38	26-29
Al ₂ O ₃	5-9	38-40	70-72
SiO ₂	19-25	4-6	less than 1
Fe ₂ O ₃	2-4	14-18	less than 1

Sorel cements are basically magnesium oxychloride and are made by mixing caustic magnesium hydroxide with a solution of magnesium chloride. The production of magnesium oxychloride is normally slow, but it can be accelerated by high temperatures or by suitable additives. Although Sorel cements are most commonly employed in the manufacture of interior floors they have been used as the cementing agent in chemically-bonded basic refractory bricks, with calcined magnesia or dolomite as aggregate.

Phosphate cements are used in dentistry for fillings and restorations. Phosphoric acid is mixed with an oxide, usually zinc, and the meta-phosphate, which forms slowly, sets to a hard mass which is very resistant to most mouth fluids.

Eugينات behave similarly to phosphates and are used for the same purposes. Although they do not set as hard as phosphate cements, eugينات are strong antiseptics and are used where the risk of mouth infections is serious.

LUTES

A LUTE is a material which acts as a bond but which does not set to a rigid body. They are used where some plasticity is required in the body to permit movement without cracking or deformation.

Lutes are used to seal structures and to prevent the escape of gas or liquors. Because of their non-rigid condition, they can be used as a seal between two parts of a structure which have different thermal expansion coefficients.

In general, luting materials do not undergo chemical change, so that any strength which they develop must be purely physical in effect. The most common example known in ceramic practice is *clay* which is mouldable when wet but hardens on drying. Most finely-divided powders can be used as lutes and they should be selected according to the purpose for which they are being used. Finely-powdered *zircon* is a valuable lute for high temperature use; *asbestos* is also commonly employed. Acid-resisting lutes are usually based on *bitumen* and such materials are used to form a cushion between ducts and pipes carrying corrosive liquids and the surrounding foundation material.

Bonds and Cements for Brickwork. Although it is often not realised, the strength of a brickwork structure is largely dependent on the cementing material which binds the bricks together. It is also true that many furnaces designed to withstand

high temperatures with perhaps a high degree of slag attack, fail because an unsuitable bond is employed. It is equally as important to select a serviceable bond as it is to choose a suitable brick and to bear in mind the conditions during use.

For *building bricks and for other architectural purposes*, the prime, but by no means the only requirement in the cement or mortar, is strength. This can usually be achieved by using a suitable mixture of sand (composed of angular grains) and either lime or Portland cement. A more pleasing effect is often produced by adding a colouring agent to the mortar so that it blends (or contrasts) with the bricks with which it is used.

The presence of free lime in a mortar can have serious and unpleasing consequences on bricks. Such material is a frequent source of efflorescence (p. 832) and in a sulphurous atmosphere, small amounts of free lime in the mortar may lead to bursting or powdering in the bricks. Mortars composed of sand and lime or cement are usually porous and not very serviceable when exposed to severe conditions of weathering. They can be improved considerably by incorporating with them small amounts of sodium silicate, tar or bitumen which are water-resistant and provide an effective weatherproofing.

Ordinary mortar should never be used to bond the brickwork in kilns or muffles where the temperature may exceed 200° C. or where there is any possibility of contact with sulphurous gases or with liquids of an acidic nature.

Bonds for use at moderately high temperatures (up to 1,000° C.) must contain a cement which is serviceable up to those temperatures, and the one most commonly employed is *ciment fondu*, which is mixed with sand or other cheap non-plastic material. Mixtures of sand or fireclay grog, plastic clay and sodium silicate are also suitable under these conditions and if the grog and clay are carefully chosen, such cements can be used up to 1400° C.

Cements containing *ciment fondu* are resistant to acids in moderate concentrations and they are not unduly attacked by sea water or by acid soils; they can be further improved by using a small amount of bitumen with them.

For bonding brickwork which has to withstand *high temperatures*, the non-plastic component must be refractory and the cement must not break down under service conditions. Many proprietary cements are available, some of which use an aluminous cement, others a plastic clay and/or sodium silicate or other bond and others employ a low refractory clay which forms a glass at the temperatures of operation. The main disadvantage of most types is that they shrink excessively at high temperature and are readily eroded by slags or high velocity gases, with the result that the brickwork is weakened and corners and edges exposed to mechanical and chemical erosion. It is thus important to restrict the amount of cement between the bricks to a minimum by using shapes which are accurately sized. *Zircon cements* are particularly valuable, because they are highly resistant to most slags at all temperatures; cements containing a proportion of *kyanite* have also proved effective at high temperatures. The advantage of the latter type of material is that it expands on heating and hence prevents the bond from shrinking away from the bricks.

CHAPTER VII

PHYSICAL AND STRUCTURAL PROPERTIES OF RAW CERAMIC MATERIALS

MANY properties of ceramic materials, both in the raw and fired states, are related to their composition, but of almost equal importance are the particle size and the shape of the minerals which are present, and, also, the way in which they are agglomerated or situated with respect to each other so as to form the *structure* or *fabric* of the material. In many ceramic bodies, the treatment and processing during manufacture produces many changes in the appearance, colour, hardness and other physical properties, but, in most cases, the original arrangement of the grains persists and can be traced in the final product. The textural properties of the final article are, thus, often largely dependent on the macroscopic or bulk-properties of the raw materials.

The physical aspects of the fabric of a material are best considered from the point of view of the properties which are a direct result. The principal of these are: (a) texture; (b) homogeneity; (c) porosity; (d) specific gravity; (e) bulk density; (f) permeability; and (g) penetrability.

Many of these properties are of equal or greater importance in the fired products and in this connection will be considered in Chapter XII.

TEXTURE

THE term 'texture' is difficult to define for it has a wide variety of meanings, and is subject to many variables, which together impart a characteristic structure to the material. These include: (a) the shapes of individual grains; (b) their sizes; (c) the grading or packing of such grains; and (d) the density or closeness of packing of the mass.

The texture is said to be *coarse* when the particles are large or loosely-spaced and *fine* when the particles are small. *Open-textured* materials are those where the individual particles are not closely packed and many large voids are present; conversely, *close-texture* implies very small voids or, in some cases, a minimum of vacant spaces.

The texture¹ of a material has a very important influence on many of its

¹ The texture of ceramic bodies, both raw and fired, can be examined by impregnating the surface with a slip of plaster of Paris and allowing it to set. If a thin slice is cut from the body and the face polished, the particle shape and the size and shape of void space (filled by plaster) can be clearly seen. A low-power microscope is an advantage when fine-textured materials are to be examined.

When the body is light-coloured, better results are given by adding a colouring agent (e.g. iron oxide) to the plaster of Paris prior to impregnation.

properties, including shrinkage, porosity, fusibility, and, in the case of clays, plasticity. Notwithstanding its importance, the texture is not considered or controlled to anything like the extent it should be, and many failures in the production and use of articles from clay and other ceramic materials are due to the lack of proper attention to this property.

The **shapes of the grains** is a prime factor in determining the texture of a material. They may be classed as: (a) flaky or platelike; (b) needle-shaped; (c) angular; or (d) rounded.

(a) **Flaky particles.** The micas and clay minerals consist of layers, which result in crystals of these minerals being typically flaky: i.e. the area of cross-section is considerably greater than the thickness. A sample of clay, especially if it has been purified from associated quartz grains, is composed of an aggregated mass of plate-shaped crystallites. When suspended in a perfectly still liquid, particles will settle in such a way as to present the greatest possible surface area to the direction of fall. Therefore clays, micaceous and similarly shaped grains will, under conditions of free sedimentation, form a mass in which all flakes are oriented in the same way, with their flat faces at right angles to the direction of fall. All sedimented clay deposits have particles arranged in this way, although the presence of quartz or other angular-grained minerals in the clay may locally disturb the ordered arrangement.

Frequently, clay deposits exhibit characteristic *bedding* or *lamination* which is often horizontal, but if faulting or folding has taken place, the beds may be inclined at an angle. Such clays easily cleave along these directions and close inspection will usually reveal the presence of a layer of micaceous flakes arranged parallel to the line of fracture.

Because the particle size is invariably small, clays are fine-textured. However, many micropores are present which are the result of the evaporation of water from between the deposited particles. Consequently, most clays are of open texture unless, at some stage in their geological history, they were subjected to compression, metamorphism or secondary precipitation.

Laminated masses are troublesome when being manufactured into ceramic shapes, for there is a tendency for such material to split along the natural lines of weakness, during firing. It is, therefore, essential to grind clays sufficiently before use so as to reduce this undesirable feature of flaky materials. Excessive grinding must be avoided as it will cause other defects in some articles.

The cleavage, on firing, of laminated clays is serious only when the flake-size is large or when the degree of compactness is great. Slip-cast clayware is composed of oriented mineral plates but flaking is uncommon except when the size of the cast body is large.

When particles of the same grain size are compared, flaky or platelike particles develop greater strength in the mass than do rounded or equi-proportioned grains. This is because the specific surface area (or surface area per unit weight) is greater and in an oriented aggregate where plates are virtually in contact along their basal section, the binding force is relatively greater than with rounded grains.

(b) **Needle or lath-shaped crystals** are common in some naturally-occurring ceramic raw materials such as halloysite clays and dolomite rocks, but the best-known example is *mullite* which is one of the main products when aluminosilicate

mixtures are fired. The texture of bodies composed of such particles depends on the orientation of individual grains, but most fibrous or needle-shaped crystal masses are of open texture. *Asbestos* which consists of regularly-arranged needles of chrysotile or amphiboles is of value as a thermal insulator largely as a result of the micropores which separate each fibre.

When lath-shaped crystals are arranged in more random fashion the resulting structure is usually strong. The crystals of mullite in fired clays are in the form of a network or felted mass of needles which interlink and intergrow throughout the body.

(c) **Angular grains** are the common form of particles in ceramic raw materials (other than clays) for they are the automatic result of crushing and grinding processes. The texture of such an agglomeration is difficult to predict, for it depends on the size distribution and the methods of packing. Where the particles approximate to cubes, the way in which they may be packed together has much in common with the arrangement of rounded or spherical particles. However, as a result of the angularity, they do not pack as readily because the 'ease of flow' is considerably less.

(d) **Rounded grains** occur in many sedimentary deposits as a result of mechanical erosion during transportation. They are a special feature of sands and gravels of marine origin where virtually all the particles are roughly spherical.

PACKING

THE packing¹ and texture of masses composed of rounded particles have been studied in detail and the results obtained have provided a valuable basis for improving the texture and quality of ceramic wares.

Where spheres of equal size are packed together, it is impossible to produce a mass with no voids. A mass with maximum porosity or open spaces will result if the spheres are arranged so that each sphere is in contact with six others (Fig. VII.1A). It will be reduced if one particle in each group of four rests equally on three others in the form of a tetrahedron (Fig. VII.1B). The extension of this unit will result in each sphere touching twelve similar ones and give rise to one of the close-packed arrangements mentioned and illustrated in Chapter II (p. 90).

The void space produced by the open and close-packed arrangements can be calculated quite simply as 48 per cent and 26 per cent respectively. (The value of 26 per cent is the same for cubic, hexagonal or one of the distorted forms of close-

¹ The ratio of the weight of a powder to the minimum volume which it can occupy is known as the *packing density*. Well-graded materials with a minimum of voids, occupy a relatively small volume, so that their packing density is not very different from their true specific gravity (see p. 403).

The packing density can be measured by placing a weighed sample of dry powder into a measuring cylinder and shaking it until a constant volume is reached. The packing density is the weight divided by this volume. A less accurate figure, although one which is of more value when the powdered material is to be moulded under pressure, is given by ramming a weighed sample in a cylinder with a plunger of definite weight (between 150 and 300 gm.) which is allowed to fall on the specimen a certain number of times (usually 50) from a fixed height in rapid succession. The volume of the shape is then measured and the packing density derived. This value is sometimes known as the *rammed density* and is important in the manufacture of ceramic materials from a semi-dry or almost dry powder. This density is expressed in gm. per cc. (or in lb. per cu. ft.).

packing although the method of calculation is different in each case). These two values are the theoretical extremes in the packing of equally-sized spheres. Tests carried out by Westman and Hugill,¹ using mono-sized spheres of different dimensions and materials have shown that the packing is virtually the same in all cases and that the system has a void space of 38 ± 1 per cent. This is intermediate in value between that of the open and close-packed arrangements and it is suggested that the

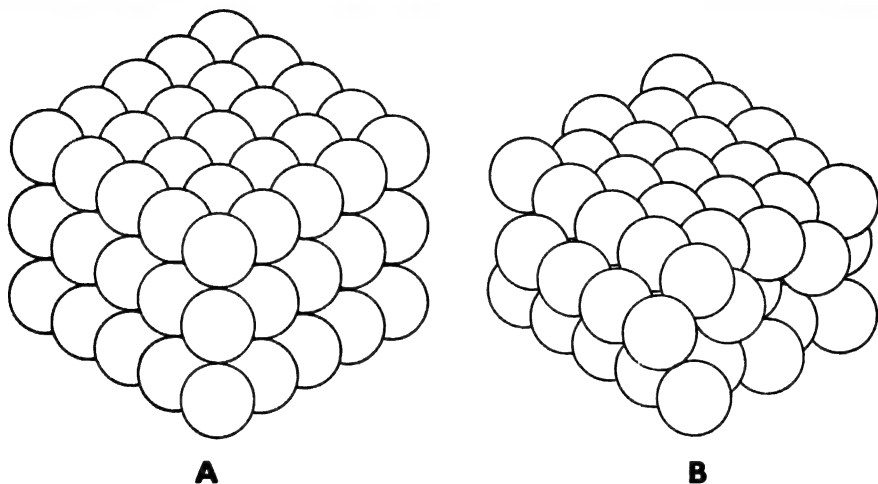


FIG. VII.1. THE PACKING OF SPHERES
(A) Open packing; (B) close packing

particles have an open structure in the vertical direction, but horizontally they are almost ideally close-packed.

The void space can be reduced by adding to the original batch of large spheres a number of smaller ones of a size which can fill the vacant interstitial positions between the large grains.

Westman and Hugill also proved that, in a system composed of spheres of two different diameters, maximum packing is secured when the larger particles are infinitely large compared with the smaller ones. This is shown graphically in Fig. VII.2, where the composition (in terms of the true volume of each size of sphere added), is related to the ratio of the actual volume of the mixture (V_a) to the true volume, which for convenience is regarded as unity. The apparent volume is related to the percentage of void space by the equation

$$V_a = \frac{100}{100 - \text{void space}}$$

Two experimentally determined graphs are shown representing the bulk volume of mixtures of differently-sized particles. As the size ratio is increased from 8:1 to 50:5:1 the minimum point in the curve is reduced, thus illustrating that, in a two-component system, maximum packing or minimum void space is reached when the

¹ Westman, A. E. R. and Hugill, H. R., *J. Amer. Ceram. Soc.*, 13, 767, 1930.

size ratio is large. The greater is the difference in the size ratio of the spheres, the smaller is the value of the bulk volume attained at maximum packing. It is possible to calculate, theoretically, the variation in bulk volume on mixing particles of two sizes when one is infinitesimally smaller than the other. The minimum percentage of voids which could result from such a mixture is 14.4, corresponding to a bulk volume of 1.19 referred to a true volume of 1.

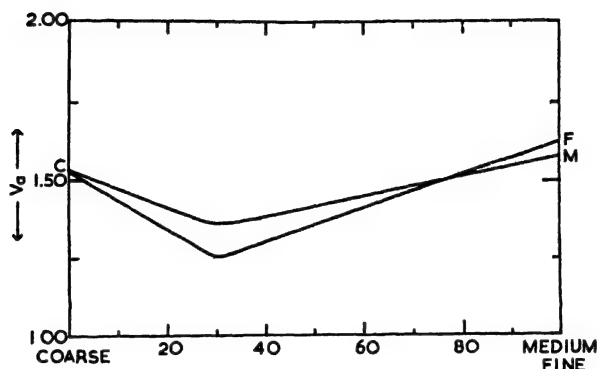


FIG. VII.2. GRAPH SHOWING THE PACKING DENSITY OF MIXTURES OF SPHERES OF TWO DIFFERENT DIAMETERS (after Westman and Hugill)

The effect of introducing particles of other sizes can be predicted by applying similar theoretical reasoning and Westman and Hugill have shown that maximum packing is produced by selecting spheres with very large diameter ratios. They have deduced that the minimum apparent volume (V_a) of a mixture of particles of three different sizes may be calculated from the equation

$$V_a = \frac{a^3}{(1-a)^3} + a^3$$

where a is the bulk or apparent volume of a system containing spheres of only one size. The assumption is made that the value of a is the same for the coarse, medium and fine particles and equal to 1.605 (corresponding to the experimentally-determined system with a void space of 38 per cent). Particles of three sizes with large diameter ratios will therefore pack together to give a mass of minimum volume 1.057 corresponding to a void space of 5.4 per cent.

This may be deduced quite simply by considering the ideal case. A system composed of single-sized particles of large size will pack together to give an average void space of 38 per cent. The introduction of particles of another size, very much smaller than the first, will result in the void space being filled, but those smaller spheres will also pack in such a way that 38 per cent of the space occupied by them will in turn be void. Therefore, the result of mixing particles of two sizes is to reduce the total void space in the system to 38 per cent of 38, i.e. 14.4 per cent. A decrease of 23.6 per cent in the total void space has been achieved so this is the theoretical volume of smaller sized grains required.

Even smaller spheres can be added to the mixture of two grades of spheres and these will occupy the remaining void space, and closest packing will result if the third size of spheres is infinitesimally smaller than the second grade, which for convenience will be called the medium fraction. The overall packing can be calculated because the smallest-sized particles occupy the 14.4 per cent of void space in the mixture of coarse and medium particles, but because they are of one size, 38 per cent of the

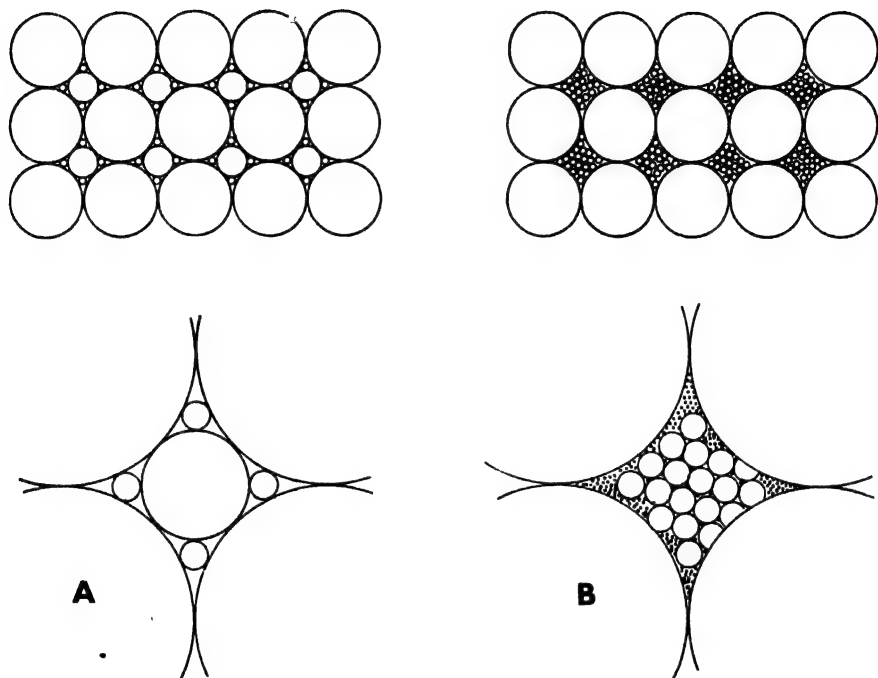


FIG. VII.3. THE PACKING OF SPHERES OF DIFFERENT SIZES
(A) Theoretical representation; (B) practical representation

total space which they occupy will be void. Therefore, in a system containing spheres of three sizes, the total void space will be 38 per cent of 14.4, i.e. 5.4 per cent. A further reduction in the voids of 9.0 per cent has taken place, hence this must be the volume occupied by the finest particles.

The theoretically predicted ideal packing of a mixture of spheres of three different sizes where the size ratio is very large, is where the mixture contains 62.0 parts of coarse, 23.6 of medium and 9.0 of fine spheres (by volume). The percentage void space in such a mixture would be 5.4 per cent.

The nearest experimental approach to this value was obtained with a mixture containing 70 per cent coarse, 20 per cent medium and 10 per cent fine spheres by volume, where the diameter ratios of the spheres were 50.5:8:1. The bulk-volume which resulted was 1.202 giving a calculated void volume of 16.8 per cent.

The classical representation of good packing using mixtures of spheres of different diameters is different. The ideal system is presumed to consist of a framework of large-sized spheres with interstices filled by slightly smaller ones which are of such a size that they touch each of the surrounding large-sized balls. The picture is completed by imagining that smaller spheres occupy the remaining void spaces which remain as shown in Fig. VII.3A.

Such a system would ideally have a very small void space, but it would be impossible to attain in practice, because the smaller-sized grains are rigidly contained in the space between large ones and are not free to move. Consequently no amount of tapping or pressing could produce the ideal arrangement from an assorted mass of randomly-arranged spheres. The work of Westman and Hugill has established that, only when the small-sized spheres are of a diameter which enables them to move freely through a network of larger grains, will there be any approach to close packing on a practical scale. The true pictorial representation of a close-packed system of spheres of two different diameters is shown in Fig. VII.3B. When even smaller-sized grains are added they occupy a similar position relative to those of medium size.

GRADING

THE mixing of spheres or particles of different diameters in various proportions so as to improve the closeness of texture and reduce the void-space is known as *grading* and has an important application in the manufacture of most ceramic bodies.

The use of graded materials is desirable for several reasons:

(a) If only coarse material were employed, it would require a very large proportion of bond to fill the voids and cement the grains together, and the resultant mass could not be so strong as a better-graded material, on account of the small number of points of contact between the 'cement' and the larger particles.

(b) The porosity and permeability are reduced in a properly graded material, and this often has a marked effect on its resistance to corrosion, abrasion, etc.

(c) The appearance and other qualities of a material may often be improved by removing particles of certain sizes from the material, as when pebbles are washed or screened from a clay or sand.

(d) The use of carefully-graded material greatly lessens the possibility of spalling, splintering, and cracking when a material or article is exposed to sudden changes in temperature.

(e) Well-graded raw material has a considerably smaller shrinkage on firing than a body containing appreciable void space, and furthermore, reactions take place more readily and proceed more rapidly in such a system, because of the greater number of points of contact.

Although the individual particles in ceramic raw materials are usually not spherical but angular or sub-angular, the general principles of grading apply, provided the grains are fairly symmetrical and not elongated in one particular direction. Thus most ground or crushed materials may be separated into size-fractions, which, by suitable blending, will give a close-packed system.

Most clays require to be crushed before being moulded into shape and may

therefore be regarded as composed of angular grains of different sizes, which if carefully graded, will give a good texture with a minimum of void space, though it must be remembered that the individual particles produced by grinding may consist of many small agglomerated crystallites.

Although angular grains may be graded by mixing particles of different sizes in suitable proportions, they do not pack as readily as rounded grains. Some degree of interlocking occurs, however, which results in an overall lower porosity.

The application of the principles of grading on an industrial scale has necessarily to be a compromise. The ideal system would be one where several grades of particles are selected with large size-ratios and the proportions of each suitably adjusted, but such a mixture could not be used in practice because of the wastage in time and material.

It is standard practice to crush the raw material and select three grades, the centre grain size of each of which should be very much smaller than that of the larger size. Various specifications have been suggested by different workers for suitable gradings to give a dense, low porosity body. Although at first sight there appears to be a divergence of opinion, closer examination shows that they are all similar and differ mainly in the definition of coarse, medium and fine grades.

The grading required to secure good packing and minimum porosity in silica brick batches made from crushed Welsh quartzite has been investigated by Hugill and Rees,¹ who suggest that the best results are obtained with the following mixture:

	<i>Coarse grade</i>	<i>Medium grade</i>	<i>Fine grade</i>
Sieve size	5-30	30-80	Through 80
Particle size range (mm.)	3.35-0.5	0.5-0.18	less than 0.18
Centre grain-size ratios	16	3	1
Percentage by weight in each range	45	10	45

Angenot,² working with fractionated natural clays, concluded that the best grading was obtained by mixing three fractions as follows:

	<i>Coarse grade</i>	<i>Medium grade</i>	<i>Fine grade</i>
Particle size (mm.)	3	0.6	0.2
Grain-size ratios	14	2.8	1
Percentage by weight in each range	36	24	40

He found that in practice such a mixture gave a higher packing density than one where the size-ratios were 25:5:1.

The closeness of texture can be controlled to some extent by careful regulation of the particle size ranges of the raw material, but the fineness or coarseness of the texture depends on the ultimate size of the largest particles. Fine-textured material must be composed of very small grains, such as exist naturally in clays and some other rocks, or they may be produced artificially by fine grinding. Many clays

¹ Hugill, W. and Rees, W. J., *Trans. Brit. Ceram. Soc.*, 28, 62, 1929.

² Angenot, P., *Verre Silicates Ind.*, 12, COBEA suppl., 17, 1947.

including china and ball clays, will readily disperse in water and pass entirely through a 200-mesh sieve (0.076 mm. aperture); but most natural clays contain larger particles of sand, mica or other minerals.

PARTICLE SIZE OF CERAMIC MATERIALS

SOIL chemists, geologists and many ceramists have adopted the Seger sub-division of the various components which are present in natural clays and other detrital deposits. This is as follows:

Clay includes all grains with a diameter less than 0.01 mm. or those washed out by a stream of water with a velocity of 0.18 mm. per second under a pressure head of 20 mm.

Silt includes all grains between 0.01 mm. and 0.025 mm. diameter, or those washed out by a stream of velocity 0.7 mm. per second.

Dust sand includes all grains from 0.025 to 0.04 mm. diameter which are washed out with a stream of water with a velocity of 1.5 mm. per second.

Fine sand includes all grains between 0.04 mm. and 0.33 mm. diameter separated by means of sieves.

Coarse sand includes all particles with a diameter greater than 0.33 mm.

Kaolins and china clays, after separation from the parent altered granite rock and associated impurities, such as quartz and mica, usually consist of particles less than 0.01 mm., but some coarser varieties are known with only 20–25 per cent of particles less than 0.01 mm. Cornish and Devon china clays contain only a small percentage of particles less than 0.0003 mm., i.e. 0.3 microns. Purified china clay has a very limited grain size range and about 95 per cent of the particles are between 0.002 mm. (2 microns) and 0.0003 mm. (0.3 microns) in size.

Sedimentary Kaolins, which have been removed from their original site and re-deposited consist of smaller particles and are much more plastic. Norton¹ has reported that Florida plastic kaolin is over 30 per cent finer than 0.0005 mm. (0.5 microns) and that particles as small as 0.05 microns may be present.

Ball clays of the best qualities contain 60 per cent or more of particles less than 0.0005 mm. and up to 90 per cent less than 0.001 mm., but many are much coarser. The larger particles in most ball clays are usually quartz, mica or some other impurity present in small amounts. The variable and often large proportion of organic matter, which is the cause of the dark colour of the raw clay, is mostly present as a film surrounding the clay particles.

The particle size of ball clays is notoriously variable and strict control over the raw material has to be exercised, because slight changes can alter its properties considerably. For this reason it is inadvisable to use a different type of ball clay in the manufacture of a ceramic body, without first assessing its behaviour.

Bentonites and montmorillonite clays are, for the most part, of extremely small size. The larger proportion of clay particles are less than 0.05 microns and those that are above this size are probably agglomerates. In a watery suspension, the ultimate particles of montmorillonite clays are probably only a few Ångstrom units in size

¹ Norton, F. H., *Elements of Ceramics* (Addison-Wesley Press Inc., Cambridge, Mass. 1952).

(1 Å unit = 1×10^{-8} cm.). Commercial bentonites often contain a proportion of non-plastic material which is of a comparatively large particle size.

The particle size of clay minerals is best measured by means of the electron microscope.

Rock clays, shales, fireclays and some other clays would have an extremely fine texture if the individual particles could be separated, but unless special methods are adopted, each 'particle' of clay separated by the action of water will be found, on examination, to consist of an aggregation of smaller grains. Articles made of such clays have a coarser and more open texture than those made from clays in which the individual grains are readily separated from each other.

Freshly-dug clays may be classified according to their texture as: (a) shales; (b) marls; (c) loams; (d) stony clays; and (e) plastic clays.

Shales have a laminated or stratified texture; they may be either fine or coarse and either rich or poor in clay as the term 'shale' has no connection with the size of the grains nor with the composition of the material.

Marls or **Malms** are natural mixtures of clay and chalk and may usually be recognised by their friable nature, their texture being quite different from that of other clays. The term *marl* is often used for materials having a similar texture, but which contain very little, if any, chalk, e.g. Staffordshire marls. The greater part of most true marls can usually be washed through a 100-mesh sieve, though coarser marls are also found.

Loams are mixtures of sand and clay; they are largely used for the manufacture of bricks, roofing tiles, floor tiles, terra cotta, agricultural pipes, and coarse (red) pottery. Their texture is similar to that of marls. Loams and marls are often confused, but they may be readily discriminated by adding a little hydrochloric acid, when a marl will effervesce, whilst a loam will not do so. The texture of many loams is such that they are excellent for the manufacture of the articles just mentioned. The sand in them prevents loams from shrinking excessively and enables articles made from them to be dried and burned without undue risk of cracking or warping. Some loams contain so much sand that they cannot be used unless they are mixed with plastic clay to produce a stronger mass. Any very coarse, non-plastic material such as pebbles and gravel in a loam must either be removed or crushed so fine that they will not do any harm when the loam is made into articles.

Stony clays usually consist of fine clay or loam mixed with stones, pebbles, or similar non-plastic material of any size from $\frac{1}{8}$ in. in diameter to large boulders. Much of the *boulder clay* which forms part of the Glacial Drift is of this nature. The coarse material must be separated from the clay or loam before the latter can be used, even for brickmaking.

Plastic clays, when suitably moist, possess a smooth oleaginous texture which is often so fine that no definite 'structure' can be seen with the naked eye. If the material is rather drier it can be seen to consist of adherent granules, but many of these appear to be much larger than the particles of clay really are, for the granules consist of aggregations of the much smaller particles of clay. Most plastic clays also contain a considerable proportion of sand and some (such as boulder clay) contain gravel and large stones. The causes and nature of plasticity are considered in a later chapter.

An excessively fine texture is objectionable, because it is usually associated with a tendency to twist or warp when the articles are being dried or burned and with an undue sensitiveness to sudden changes in temperature. In order to eliminate the less desirable features of fine-textured clays amounts of coarse non-plastic material are often added. This may be sand or alumina but more usually it is previously-calcined raw material, called 'grog', which forms a rigid skeleton within the body and thus prevents undue shrinkage or warping during drying and firing.

For *bricks*, *roofing tiles* and *drain-pipes* the ground clay should be free from particles larger than No. 22-mesh, though for some common building bricks as much as 10 per cent of particles 0.125 in. in diameter may do no harm.

If sand is to be added to the clay it should usually consist of grains between 30- and 120-mesh. Much finer sand is seldom satisfactory though a small proportion of it is not likely to be detrimental.

For *refractory materials*, clays which will not pass through a No. 24-mesh sieve are usually too coarse, and a large proportion should pass through a No. 40- or No. 50-mesh.

If *grog* is to be added it should be of three grades: (a) *coarse grog* consists of particles between 0.125 in. and 0.375 in.; (b) *medium grog* consists of particles between 0.06 in. and 0.125 in.; and (c) *fine grog* consisting of particles between 0.03 in. and 0.06 in. in diameter.

Some manufacturers use a small proportion of much finer grog, but with some clays this creates difficulties by rendering the goods more sensitive to sudden changes in temperature.

For *fine earthenware*, *stoneware* and *china ware* the whole of the materials should pass completely through a No. 120-mesh sieve and a large proportion should pass through a No. 200-mesh sieve. For some of the finest porcelains the whole of the materials will pass readily through a No. 200-mesh sieve.

Glazed sanitary ware may be made of clays containing a moderate proportion of particles 0.02 in. in diameter, provided that there is at least 50 per cent fine enough to pass through a No. 72-mesh sieve.

All these suggested sizes are necessarily approximate and the grades of the various materials must always be selected with regard to their type and quality and to the requirements of the individual user.

Ceramic raw materials other than clays usually have a medium or coarse texture, unless they are ground excessively finely. Such mixtures are non-plastic and careful grading is essential if the body is to be strong on moulding and firing. Quite often a finely-grained plastic material, such as clay, or an organic substance, e.g. sulphite lye, is added as a bond. Thus, *silica bricks* are chiefly made of a mixture of three grades of silica: (a) particles between 0.125 in. and 0.185 in.; (b) particles between 0.04 in. and 0.125 in.; and (c) particles less than 0.04 in. in diameter but free from those less than 0.003 in. Some firms prefer to use no particles larger than 0.06 in., and include up to 30 per cent of particles less than 0.006 in.

For silica bricks accurate grading is very important because only $1\frac{1}{2}$ –2 per cent of lime is used as the binding agent (see also p. 374).

For *magnesite* and *dolomite* bricks, about 75 per cent of the particles may be less than 0.125 in. diameter and a further 25 per cent less than 0.006 in.

Chesters¹ has stated that the grading of a brick batch used in the manufacture of stable dolomite bricks is 55–75 per cent coarse, 15–5 per cent medium and 40–20 per cent fine particles, but the range of sizes in the various grades is not given.

For *bauxite bricks* the coarsest particles should not exceed 0.25 in. nor be less than 0.05 in. and the fine constituent should usually be about 15–30 per cent of finely-ground fireclay, all of which could pass through a No. 60-mesh sieve.

Glass-melting Tank Blocks require a coarse texture of low penetrability such as is produced by a mixture of

$$\begin{array}{l} (a) \\ (b) \end{array} \text{ Particles } \left\{ \begin{array}{l} 0.125 \text{ in.} - 0.25 \text{ in.} \\ 0.062 \text{ in.} - 0.125 \text{ in.} \\ 0.031 \text{ in.} - 0.062 \text{ in.} \end{array} \right\} 1 \text{ part by volume}$$

for the bottom blocks, whilst for replacement flux-line blocks the proportions may be 2:2:1.

Blocks for *muffles* and *retorts* should be made of the coarsest practicable material so graded as to be impermeable to gases. For gas-retorts a coarse grog and moderately fine fireclay is best.

THE MEASUREMENT OF PARTICLE SIZE

As the texture of raw materials is intimately related to the particle size distribution, if some control is to be exercised, it is important to determine the sizes of grains present and the proportions of each size.

The methods available are many, although when the particle size is large (greater than 0.0025 in. or 0.006 cm.) *screening* or *sieving* is probably the best.

Sieving, Sifting and Screening involves passing the material—either in its dry state or in suspension in water—over a series of meshes each having apertures of known dimensions. The particles larger than these apertures remain on the sieves, whilst the smaller particles pass forward to sieves with successively smaller apertures until the last one is reached, through which the smallest grains eventually pass. This method is very convenient for separating all particles larger than 0.0025 in. diameter (200-mesh), but is seldom applicable to smaller ones on account of the difficulty of making accurate sieves with smaller apertures.

Sieves, riddles, and screens are made with apertures of various shapes some of which are circular, others square, and still others are rectangular. The last-named are useless for investigating the texture or fineness of a material.

Sieves with circular apertures are simply perforated sheets of metal or other suitable material and are not as reliable for testing angular materials as those with square apertures made from wire-gauze.

Gauze-sieves are made of various metals, including iron, steel, brass, bronze and occasionally copper. In some cases, gauzes made of silk (*lawns*) are employed for the finest materials, but they are very delicate and not to be recommended for bulk separation. Those made of phosphor-bronze are usually the most satisfactory. All sieves used for testing should be examined frequently to ensure that the apertures remain of the desired sizes, as otherwise the results obtained may be erroneous.

¹ Chesters, J. H., *Steelplant Refractories* (The United Steel Companies Ltd., Sheffield, 1946).

This applies particularly to sieves with the finest apertures which tend to stretch and sag with frequent use.

Standard sieves are in use in both this country and abroad; they are classified by numbers which designate the number of apertures per linear inch, although the actual sizes of holes can be derived only provided that the diameter of the wire used is known. The four types commonly employed are: (a) British Standard Test Sieves (B.S.S.) conforming to the British Standard Institute Specification (No. 410, 1931). (b) Institution of Mining and Metallurgy (I.M.M.) standard, in which the apertures are so designed that they are related to the sieve number (x) by the factor $\frac{1}{2}x$; (c) Tyler Standard Screens; and (d) The United States Standard Sieve Series. The last two are those commonly used in the United States and in both the ratio of the aperture of any particular screen to that of the succeeding one is equal to $\sqrt{2}$ or 1.414.

The aperture-size (or length of square side) of the sieves of each series is shown in Table VII.I.

The grain-size distribution of a sample may be estimated by sieving either in the dry state or after it has been mixed with a large amount of water to form a slip or slurry. Whilst the results obtained may be quite different, the method of using the sieves is similar in each case.

A weighed quantity of the sample is placed in the largest-aperture sieve and stirred or shaken until as much of it as will pass through that sieve has done so. The material which has passed through the first sieve is similarly treated on the next finer sieve in the series and this process is continued either until all the powder is removed or no smaller sieves are available. The particle-size distribution may then be calculated by plotting the cumulative curve of the percentage of sample retained by each sieve against the size of aperture.

The dry method of sieving will indicate the fineness of division after crushing or grinding, although some particles retained on the sieves will be aggregates of much finer crystallites. When the size-distribution is being measured to assess the textural properties of the moulded powder it is usually advisable to regard such agglomerated particles as single grains. If, however, the particle size of the crystal or mineral fragments is required then such composite grains must be broken down and for this reason the 'wet' method of sieving is preferable when an ultimate size analysis is required. The residue retained on each sieve can be readily freed from adhering finer particles by washing with a jet of water.

Even with prolonged treatment, some large particles of particularly hard clays remain as agglomerates; these are extremely difficult to break up and as they would certainly behave as single particles when being moulded into shape they are usually recorded as such in the particle size analysis. As a result, fireclays, clay-shales and similar materials appear to contain a larger proportion of coarse particles than would be expected. When the ultimate crystallite sizes are required, all agglomerates must be broken down but without disrupting any individual crystal.

Many raw materials, particularly clays, contain particles which pass through the smallest-aperture sieve. The estimation of the grain-size distribution of such materials is often assessed by water sedimentation or elutriation methods, although these are far from reliable in many cases.

TABLE VII—I. SIZE OF APERTURES IN STANDARD SIEVES SERIES

<i>Number of Series</i>	<i>B.S.S.</i>	<i>I.M.M.</i>	<i>Tyler Series</i>	<i>U.S. Standard</i>
	From 2 in. to $\frac{1}{4}$ in. in $\frac{1}{8}$ in. steps then $\frac{3}{16}$ in., $\frac{1}{4}$ in., $\frac{1}{8}$ in. and $\frac{1}{16}$ in.	in.	in. 1-050 0-883 0-742 0-624 0-525 0-441 0-371 0-312 0-263 0-221 0-185 0-156 0-131 0-110 0-093 0-078 0-065 0-055 0-046 0-0390 — 0-0328 — 0-0276 — 0-0232 — 0-0195 0-0164 — 0-0138 — 0-0116 — 0-0097 0-0082 — 0-0069 — 0-0058 0-0049 — 0-0041 — 0-0035 0-0029 — 0-0024 — 0-0021 — 0-0017 —	in. 0-315 0-265 0-223 0-187 0-157 0-132 0-111 0-0937 0-0787 0-0661 0-0555 0-0469 0-0394 0-0331 — 0-0280 — 0-0232 — 0-0197 0-0165 — 0-0138 — 0-0117 0-0098 0-0083 0-0070 — 0-0059 0-0049 0-0041 0-0035 0-0029 0-0024 — 0-0021 — 0-0017 —
2 $\frac{1}{2}$	—	—	0-312	0-315
3	—	—	0-263	0-265
3 $\frac{1}{2}$	—	—	0-221	0-223
4	—	—	0-185	0-187
5	0-1320	0-1000	0-156	0-157
6	0-1107	—	0-131	0-132
7	0-0949	—	0-110	0-111
8	0-0810	0-0630	0-093	0-0937
9	—	—	0-078	—
10	0-0660	0-0500	0-065	0-0787
12	0-0553	0-0417	0-055	0-0661
14	0-0474	—	0-046	0-0555
16	0-0395	0-0313	0-0390	0-0469
18	0-0336	—	—	0-0394
20	—	0-0250	0-0328	0-0331
22	0-0275	—	—	—
24	—	—	0-0276	—
25	0-0236	—	—	0-0280
28	—	—	0-0232	—
30	0-0197	0-0167	—	0-0232
32	—	—	0-0195	—
35	—	—	0-0164	0-0197
36	0-0166	—	—	—
40	—	0-0125	—	0-0165
42	—	—	0-0138	—
44	0-0139	—	—	—
45	—	—	—	0-0138
48	—	—	0-0116	—
50	—	0-0100	—	0-0117
52	0-0116	—	—	—
60	0-0099	0-0083	0-0097	0-0098
65	—	—	0-0082	—
70	—	0-0071	—	0-0083
72	0-0083	—	—	—
80	—	0-0063	0-0069	0-0070
85	0-0070	—	—	—
90	—	0-0055	—	—
100	0-0060	0-0050	0-0058	0-0059
115	—	—	0-0049	—
120	0-0049	0-0041	—	0-0049
140	—	—	—	0-0041
150	0-0041	0-0033	0-0041	—
170	0-0035	—	0-0035	0-0035
200	0-0030	0-0025	0-0029	0-0029
230	—	—	—	0-0024
240	0-0025	—	—	—
250	—	—	0-0024	—
270	—	—	0-0021	0-0021
300	0-0021	—	—	—
325	—	—	0-0017	0-0017
350	0-0017	—	—	—

Sedimentation Analysis. The rate of fall of particles in a liquid medium was investigated by Stokes in 1845.¹ He was able to derive an equation which related the velocity of fall to the square of the diameter of perfect spheres when subjected only to the influence of gravity and free from interference by neighbouring particles.

This full expression which is called Stokes' law is

$$V = \frac{2 (\rho_1 - \rho_2) g r^2}{9 \eta}$$

where V is the velocity of fall in cm. per sec.,

η is the viscosity of the liquid $\left(\begin{array}{ccc} 10^\circ \text{ C.} & 20^\circ \text{ C.} & 30^\circ \text{ C.} \\ \text{water} = & 0.013, & 0.010, & 0.008 \text{ poises} \end{array} \right)$

ρ_1 and ρ_2 are respectively the density of the particles and the liquid medium,

g is the gravity constant (981 cm./sec.²),

and r is the radius of particles in cm.

Stokes' equation is applicable only when it is assumed that:

(a) The particles of solid matter are much larger than the particles of liquid so that the effects of Brownian movement (see p. 428) are not serious.

(b) The liquid is homogeneous and of infinite extent in comparison with the particles.

(c) The particles are smooth and rigid.

(d) No slipping occurs between the particles and the liquid.

(e) The velocity is not too great or else free settling may be restricted.

(f) The particles are small, but not excessively so.

(g) The particles are free to fall. If the settling vessel is narrow and the suspension is concentrated, the walls and the presence of neighbouring particles will affect the rate of falling. The influence of other particles is most serious, because, when suspended in a water medium, each particle becomes charged and complex repulsive forces may prevent free fall (see Chapter VIII). Oden² has shown that particles fall freely only if the concentration does not exceed 1 per cent, but serious error does not arise provided that less than 5 per cent by weight is present.

(h) The particles are true spheres. This is rarely the case and the shape factor introduces serious error. Some attempt at a compromise has been introduced by coining the term *equivalent spherical diameter* (e.s.d.). This refers the dimension of a particle to the radius of a sphere which would settle with the same velocity.

(i) The temperature of the medium is constant, as the viscosity diminishes with an increase in temperature. The velocity of fall is 30 per cent greater at 20° C. than at 10° C.

(j) There are no currents in the medium.

(k) There is no overlapping in sizes due to excessive concentration which might result in finer particles being carried down underneath larger ones. This may be largely avoided by repeated sedimentations of each fraction.

Other factors which also influence the correct determination of the particle-size distribution by sedimentation methods, are the presence of particles of different

¹ Stokes, *Camb. Phil. Trans.*, 8, 287, 1845 and 9, 8, 1851.

² Oden, S., *Int. Mitt. Bodenk.*, 5, 257, 1915.

densities (e.g. sand, chalk or clay) and associated soluble salts, organic and inorganic colloids.

From the foregoing it will be realised that the use of Stokes' Law may give results which have little relation to the absolute particle-size distribution. However for comparative determinations, methods based on the standard equation are invaluable and are used extensively.

Sedimentation tests may be carried out in several ways but they usually involve allowing a mixture of particles to settle for certain periods of time and then measuring either the amount removed from or remaining in suspension. Stokes' equation can be modified by assuming that the velocity of fall (V) is equal to the height (s) through which the particles (of radius r) fall in unit time.

i.e.
$$V = \frac{s}{t}$$

The equation then becomes
$$\frac{s}{t} = \frac{2}{9} \frac{(\rho_1 - \rho_2)gr^2}{\eta}$$

For a particular powder sedimenting at a constant temperature ρ_1 , ρ_2 , η and g are constants. Therefore the equation may be written in terms of the diameter of particles as

$$\frac{s}{t} = Cd^2$$

where d is the diameter and C is a constant, or

$$d = k \sqrt{\frac{s}{t}}$$

where k is a constant.

For material with a density of 2.6 settling in water at 25° C. (when $\eta = 0.01$), k has the value of 13.84×10^{-4} (where d is in cm. and t in minutes). Table VII.II shows the time taken to fall a fixed distance and also the distance fallen in one hour for differently-sized particles.

TABLE VII—II. SEDIMENTATION DATA FOR SPHERICAL PARTICLES OF DENSITY 2.6 IN WATER AT 25° C.

Size of Particles		Time to fall 20 cm.	Distance fallen in 1 hr.
mm.	in.		
0.1	0.004	15 secs.	3139 cm.
0.05	0.002	1 min. 31 secs.	784 cm.
0.01	0.0004	38 min. 15 secs.	31.39 cm.
0.005	0.0002	2 hr. 33 min.	7.84 cm.
0.001	0.00004	63 hr. 45 min.	0.314 cm.
(10 microns)			

Particle-size distributions may be measured by either of two *sedimentation* methods.

(a) Involves making up a slip of known concentration, carefully pouring a small volume of it on to the top of a column of water and then allowing the particles to settle for pre-arranged periods of time. The amount settling or that remaining in suspension can be estimated and related to the particle size by using Stokes' equation.

This is the principle of the *sedimentation balance*, which has been devised to measure the particle-size distribution in the sub-sieve range. The powder in suspension is allowed to fall through a column of water and settle on the pan of a torsion balance. The amount of powder which settles on the bottom of the sedimentation tube can be continuously and accurately measured, because the torsion wire carries a pointer fitted with a graticule, the image of which, on a ground-glass screen, can be observed through a telescope. The weight-size distribution can be calculated provided that the specific gravity of the powder and the specific gravity and viscosity of the liquid (water) are known. The apparatus was developed by W. Bostock¹ and is now being produced commercially; it is capable of determining the particle-size distributions of powders within the range 5 to 75 microns, but if no large particles are present, the lower limit can be extended to 2 microns.

(b) A more commonly-used procedure is to make up a suspension of the sample in a cylindrical vessel and then allow it to settle. Samples of the liquid at a fixed distance from the surface are withdrawn by a pipette at suitable intervals. An apparatus designed by Andreasen and Lundberg² to simplify this procedure is shown in Fig. VII.4.

A dilute suspension which should be entirely dispersed is contained in the graduated cylinder and filled up to the mark E. A 10 ml. pipette A is connected through a two-way tap B to a stem D by which liquid can be drawn from the level F which is exactly 20 cm. below E. The alternative outlet C to the tap allows a sample which has been collected in the pipette to be transferred to a weighed dish.

Samples should be withdrawn from time to time and the concentration at the point F determined by weighing the dried residue in the collecting dishes. The maximum grain size which remains in suspension can be calculated by applying Stokes' Law, and a graph of the percentage of original sample remaining in suspension below each maximum grain-size may be drawn. More information may be derived by constructing a histogram from the curve, thereby indicating the concentration of particles in several size ranges.

Each sample collected contains particles of all sizes, from the largest remaining above the level F, to the smallest which were present originally. Particles of one particular size (d_1) will, at the start of the experiment, be distributed uniformly through the volume of the suspension. They each must fall with the same velocity, hence their concentration round the level F will be constant until such time as those which were at level E have fallen through 20 cm. No more particles of this size can

¹ Bostock, W., *J. Sci. Instrum.*, 29, 209, 1952.

² Andreasen, A. M. H., *Ing. Skrifter*, No. 3, 1939. Andreasen, A. M. H. and Lundberg, J. J. V., *Ber. deut. keram. Ges.*, 11, 249, 1930.

then be drawn into the pipette on sampling, hence the overall concentration will be lowered, for only particles less than d_1 will remain in suspension.

The results are best represented on a graph plotting the concentration of the withdrawn samples relative to the original concentration, against the maximum size of particles which can still be in suspension at the time of sampling. For accurate results, a correction must be applied to allow for the reduction in the length of the

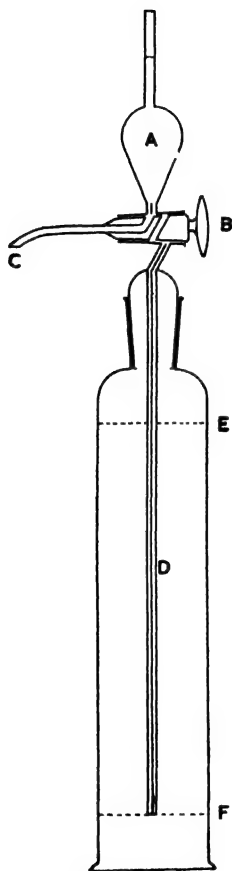


FIG VII.4. THE ANDREASEN PIPETTE

settling column when a sample is removed. A graph of the percentage weight of the sample finer than a particular size (plotted on a cumulative basis) against the particle diameter is shown in Fig. VII.5, but a clearer picture of the size-distribution of particles is given by constructing a histogram. This shows the percentage by weight of particles in a certain size-range and is a measure of the slope of the line. It is readily constructed by determining the percentage by weight of particles over small increments of size. Thus, in the cumulative curve in Fig. VII.5, the percentage of

the particles between 0–2 microns is 7 per cent, between 2–4 microns it is 29 per cent and so on, and from these values the block diagram can be constructed.

Curves of this type show that whilst clays contain particles of a wide size range, the major portion is concentrated between narrow limits.

The principle of sedimentation is used in a simple apparatus for determining the clay content of sands. The weighed sample of sand is agitated in a specified volume of water in a beaker-like container. When the stirrer is removed the particles

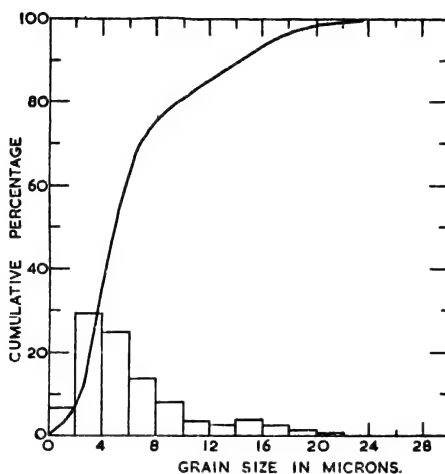


FIG. VII.5. THE GRAIN-SIZE DISTRIBUTION OF A CLAY, SHOWING THE CONSTRUCTION OF A DISTRIBUTION HISTOGRAM

fall freely and are allowed to do so for a period of time sufficient to settle all grains above 0.010 mm. The suspension is then carefully siphoned off, more water added and the process repeated a sufficient number of times to give a clear liquid after the specified settling period. The sand which remains as a sediment is thoroughly dried and reweighed; the loss in weight is a measure of the clay content. Apparatus of this type is manufactured commercially and the makers usually specify the most suitable conditions for the test.

Interesting and valuable refinements to the pipette method of sedimentation analysis are:

(i) Instead of withdrawing samples of the suspension at a fixed depth, a hydrometer or small 'diver' of suitable density is inserted into the liquid, where at some point it reaches equilibrium and then proceeds to fall steadily at the rate of sedimentation of the largest particles at that level. The use of small divers, made of hollow glass spheres weighted with metal shot to give the required density, was developed by Berg¹ and appears to be of more value than other methods using large hydrometers.

¹ Berg, S., *Trans. Int. Ceram. Congress* (Holland, 1948), p. 152.

(ii) By measuring the optical density of the suspension at certain points. A narrow beam of light is passed through the liquid and the intensity of transmitted light measured by a photo-electric cell. As large particles settle out from the section being examined the optical density decreases and a graph may be plotted of size-distribution once the apparatus has been suitably calibrated.¹

Johnson has compared the various methods of assessing the particle size distribution of some ceramic powders, and critically surveyed their limitations and advantages.²

Centrifugal Separation. As Table VII.II shows, the rate of settling of small particles is extremely slow but this can be accelerated by increasing the gravity constant (g) by means of a centrifuge.

Small-scale equipment can be used which gives up to 40,000 g and by using a controlled feed the process of separation can be made continuous. The calculation of the grain size distribution of finely divided clays is made possible by using a super-centrifuge, the details of which are shown in Fig. VII.6. The suspension enters through a nozzle at the lower end of the rotor at a controlled rate. A steam-driven turbine rotates the bowl at speeds up to 40,000 revs. per min., resulting in the separation of particles along the walls of the cylindrical rotor. The clarified liquid passes out through holes in the top of the bowl into the extracting funnels and then into a suitable receptacle. Under carefully-controlled conditions, the material in suspension can be separated into layers of gradually-decreasing particle size along the length of the rotor, so if a removable liner is inserted beforehand the grain size distribution of the sample under test can be more readily assessed by cutting the liner into strips of calculated thicknesses and weighing the amount on them.

The calculation of the size of particles separating out in a centrifuge is complicated. The increase in g is the result of the angular velocity of rotation ($\omega^2 r$) which in turn depends on the distance between the particle itself and the axis of rotation. If the column of liquid through which the particle settles is not very small with respect to the diameter of the bowl or rotor, then r will be constantly changing and an ever-increasing gravitation force will be acting on each individual particle.

Even greater complexity is introduced into the calculation of the settling position of particles sedimenting under conditions of continuous flow in a super-centrifuge. In addition to being under the influence of a constantly varying g , each particle is moving upwards with a velocity governed by the rate of flow. Saunders³ has prepared nomograms whereby the particle-size distribution of finely-divided clays can be determined and he has shown that fairly mono-dispersed size fractions can be separated.

Elutriation Methods. Particles of different sizes can be separated by suspending them in a medium, such as water, which is flowing at such a velocity that the smallest or lightest are carried away whilst the largest or densest ones settle to the bottom of the vessel. In calculating the velocity of flow to remove particles below a certain size, Stokes' Law is employed; the rate of fall of particles under gravity has to be

¹ Rose, H. E., *Engineering* (London, 1950), 169, 350.

² Johnson, R., *Trans. Brit. Ceram. Soc.*, 55, 237, 1956.

³ Saunders, E., *Ind. Eng. Chem. (An.)*, 20, 380, 1948.

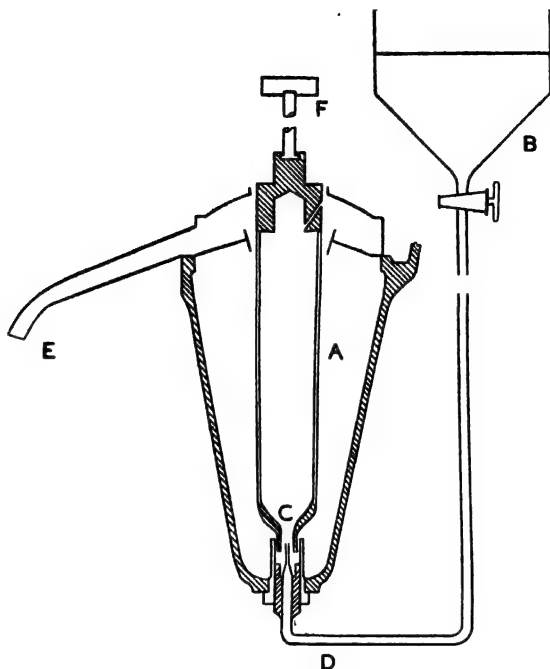


FIG. VII.6. THE CONTINUOUS SUPER CENTRIFUGE

- (A) The outside protective case
- (B) The feed reservoir
- (C) The rotor
- (D) The lead in for the suspension
- (E) The outlet for the liquid
- (F) The driving-head for the rotor

slightly exceeded by the upward flow of liquid which must be regular and uniform and free from eddying effects.

The same disadvantages which were encountered in sedimentation analysis also apply in elutriation. Grains of a flaky character are carried away by a current which is capable of removing only much smaller particles of a spherical or cubical form; similarly-sized particles but of a different density will not be removed under the same conditions. Elutriation is of value, however, because it enables fairly mono-dispersed fractions (i.e. samples containing particles of only one size) to be obtained, although large volumes of liquid are required especially when the particle size is comparatively large.

The elutriator is usually of cylindrical shape and designed so that water flows upwards through a porous plug on which rests the powder. The particles in suspension are taken off at the top of the cylinder and either allowed to settle or are evaporated to dryness. A constant flow of water must be maintained until a clear liquid is being extracted at the exit end of the elutriator; the rate of flow may then be increased and a larger-sized fraction collected.

The particle size of material being removed at a particular rate of flow can be calculated provided that the bore of the elutriator is known and also the density of the sample.

The velocity of flow of water (V) = rate of flow (i.e. volume (v) per unit time (t) \times area of cross-section (A)

$$\text{i.e. } V = \frac{dv}{dt} \cdot A$$

The velocity at which particles fall when suspended in a medium is predicted by Stokes' equation (p. 382), and for a particular size of particle to be extracted in the elutriator, its rate of fall must be slightly less than the velocity of flow of the liquid. Hence:

$$\frac{dv}{dt} \cdot A = \frac{2 \cdot (\rho_1 - \rho_2) g r^2}{9 \eta}$$

Therefore, as all other factors are known or can be calculated, the grain size distribution of a powder can be derived. The rate of flow of water is easily determined by measuring the quantity which is collected at the take-off of the elutriator over a certain period of time. It should be expressed in millilitres per second.

A basic type of elutriator is shown in Fig. VII.7. It is in common use for estimating the clay content (i.e. particles less than 0.010 mm.) in sands, but it is capable of general application. It consists of a glass vessel about 60 cm. high, the upper 10 cm. (D to E) being cylindrical and about 5 cm. internal diameter, and the lower part (E to F) conical and tapering from 5 cm. internal diameter to 5 mm. diameter. The lower end is connected to a tube G, 5 mm. in diameter, through which the water or other elutriating fluid enters and flows upwards through the apparatus. This narrow portion is necessary to ensure a truly central flow, which is quite free from eddies and side currents. The top of the elutriator is constricted so as to hold a rubber stopper carrying the overflow-tube A, which also acts as a manometer and enables the velocity of the liquid to be measured at any moment. At B in this tube is a small hole, 1.5 mm. in diameter, the edges of which have been rounded by fusion so as to provide a smooth aperture.

The pressure tube (I) should be made of barometer tubing, and should be carefully tested to see that it is really uniform. The bends at A and B must be very carefully made, so that no narrowing of the internal bore occurs. The upper vertical part of the tube is about 1 metre long and should be divided into cm., and the lowest ten of these divisions should be sub-divided into mm. The end H is connected to a water tank, or, preferably, to a large Marriott bottle, so as to maintain the water at a constant rate of flow, the volume of water being regulated with a small pinch-cock. A small piece of wire gauze is fitted into the bottom of the conical portion at F, by means of a perforated cork, in order to prevent any coarse particles from becoming stranded in the bend C.

The stopper and pressure-tube are removed and the vessel is filled to the middle of the cylindrical portion with water, and the water is allowed to flow at the pre-arranged rate. A weighed quantity of the material to be examined (e.g. 10 grams) is then placed in the vessel. If necessary, it may be transferred by the aid of a little

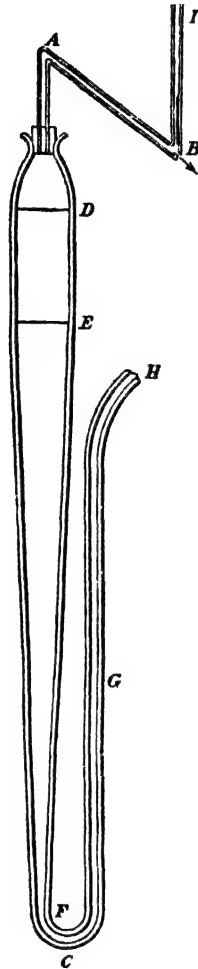


FIG. VII.7. SCHOENE'S ELUTRIATOR

water. The pressure-tube is rapidly inserted and a large pan placed ready to receive the overflow. The supply of water is continued until no further particles are carried away in suspension, after which the apparatus is dismantled, the residual matter is carefully removed, collected in a small basin, dried and weighed as 'silt'. It is not usual to attempt to dry and weigh the 'clay' portion, unless this is required for some other purpose.

The elutriator should be carefully calibrated before use and the height of the water in the pressure-tube which corresponds to the required velocity, should be ascertained. The area of the cylindrical portion D-E is ascertained by filling the apparatus with water exactly to the level E, and then running in water from a burette or from a weighed vessel until it is exactly at the point D; the volume in c.c.

or weight in grams of the water so added, divided by the height h in cm., gives the area (A) of the apparatus at the point of minimum velocity. To ascertain the rate of flow, the apparatus is set to work without any solid material and the quantity of water flowing through it in a period of exactly sixty seconds is measured or weighed, the height of the water in the pressure-tube being carefully noted. The weight or volume of the effluent water divided by the area (A), and by 60, gives the rate of flow in cm. per second. If it is either faster or slower than is required, the pinch-cock which controls it must be adjusted and another trial made. After the correct rate has been obtained, it is only necessary to note the height of water in the pressure-tube and to maintain the water at this height throughout all future tests with the same apparatus.

If the same vessel is to be used for separating particles of different sizes, a record of the height of the water in the pressure-tube corresponding to such sizes should be kept. Various other patterns of elutriator are in use, but the general principle is the same in all.

Air-separation or **air-elutriation** methods, in which air is used instead of water, are based on the same general principles, but accurate results are difficult to obtain, because convection and eddy effects are not easy to eliminate, and these destroy the steady flow conditions so necessary for quantitative determinations. Apart from this, however, air has the advantages of separating much finer particles and delivering them in a much more convenient condition. It can be used only for dry powders.

Methods of determining the grain-size distribution of a powder which are based on the settling of particles in a liquid are subject to errors which arise mainly as a result of the shape factor and the mutual interaction between liquid molecules and particles of small size.

The influence of the shape of particles on sedimentation behaviour has been studied by several workers in recent years. Davies¹ has shown that under certain conditions, factors can be applied to correct the standard equation, although if more than one type or shape of particle is present in a heterogeneous mixture a complete solution is impossible.

Absolute measurements of the size and shape of grains are best made by means of a **microscope**. Both optical and electron microscopes may be used, depending on the ultimate size of the sample. By the use of integrating scales and calibrated grids not only may the size of particles be measured, but also the proportions of each (for more details see Chapter V).

The microscopic examination of a powder with a wide range of particle sizes is much simplified if prior separation into fairly mono-dispersed grades is effected by sedimentation analysis. Should the size range be exceptionally large, a true analysis may only be possible by the use in succession of sieves, sedimentation, optical and electron microscopic methods. The range of sizes over which the various methods are effective is summarised in Table VII.III.

¹ Davies, C. N., *Symposium on Particle Size Analysis* (Inst. of Chem. Ind. and Soc. Chem. Ind., 1947), p. 25.

TABLE VII—III. THE LIMITS OF PARTICLE SIZE FOR VARIOUS METHODS OF MEASUREMENT

<i>Method</i>	<i>Approx. smallest size of particles</i>
	microns
Sieving	50
Sedimentation and elutriation (normal g)	2
Centrifugal separation	0.05
Optical microscope	0.1
Electron microscope	0.01

COMPARISON OF DIFFERENT TEXTURES

MANY attempts have been made to find a single figure or a simple diagram to represent different textures and so form a means of comparison. No single *fineness figure* can be wholly accurate and no diagram can yield all the desired information 'at a single glance' but both are of great importance when clays and other materials containing particles of many different sizes are to be compared. These are commonly understood as showing the 'distribution' of the different sizes and, though this term is not wholly suitable, it is widely used.

The proportions of the various particles of different sizes in a clay or other ceramic material are known collectively as the *particle-size distribution*. As such materials usually contain particles of many different sizes the size-distribution can be expressed only approximately but its importance is so great that even an arbitrary figure is of value.

The particle-size distribution may be represented in several ways of which the chief are:

- (i) A *graph* or *curve* in which the distribution is represented by a single line.
- (ii) A *surface factor* in which the distribution is represented by a single figure.

The *size-distribution graph* (Fig. VII.8) generally used is based on a suggestion by P. H. Boswell and is often known as a *cumulative percentage graph*.

In it, the sizes of the particles are shown on a horizontal logarithmic scale and the cumulative percentages are shown on the vertical scale. On this type of graph, a material consisting wholly of particles of one size is shown by a vertical line (AB, CD, EF and GH) which represent respectively a gravel consisting wholly of particles 2 mm. in diameter, a sand consisting wholly of particles 0.25 mm. in diameter, a silt of particles 0.04 mm. and an extremely fine clay.

When particles of various sizes are plotted on such a graph, the closer the line is to the vertical the more nearly uniform or monodispersed is the grading. Thus, the curve T-U represents a prepared sand in which nearly all the particles are the same size, W-X a sample of London clay containing 25 per cent of sand, 45 per cent of silt and 30 per cent of clay and the curve YZ a glacial clay containing no sand, 18 per cent of silt and 82 per cent of clay and rock-flour.

Curves representing several different samples can be plotted on one graph and comparison is thereby facilitated. The limits or range of sizes of the terms 'sand',

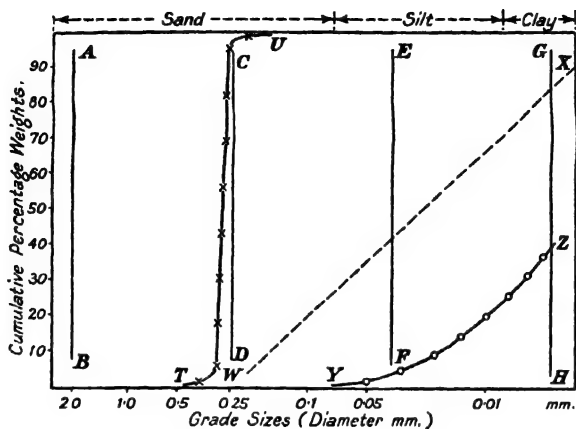


FIG. VII.8. BOSWELL'S GRADING GRAPH

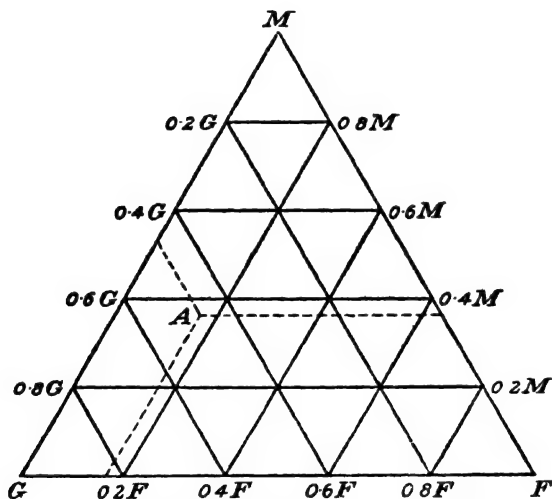


FIG. VII.9. FERET'S TRIANGULAR DIAGRAM

'silt' and 'clay' are shown at the top of Fig. VII.8 and are those suggested by Boswell. They differ (except for clay) from those on p. 375.

In Feret's *triangular diagram* (Fig. VII.9) only three sizes of particles are considered, viz:

G = particles of 2–5 mm. diameter

M = particles of 0.5–2.0 mm. diameter

F = particles less than 0.5 mm. diameter,

but any other size-groups may be used.

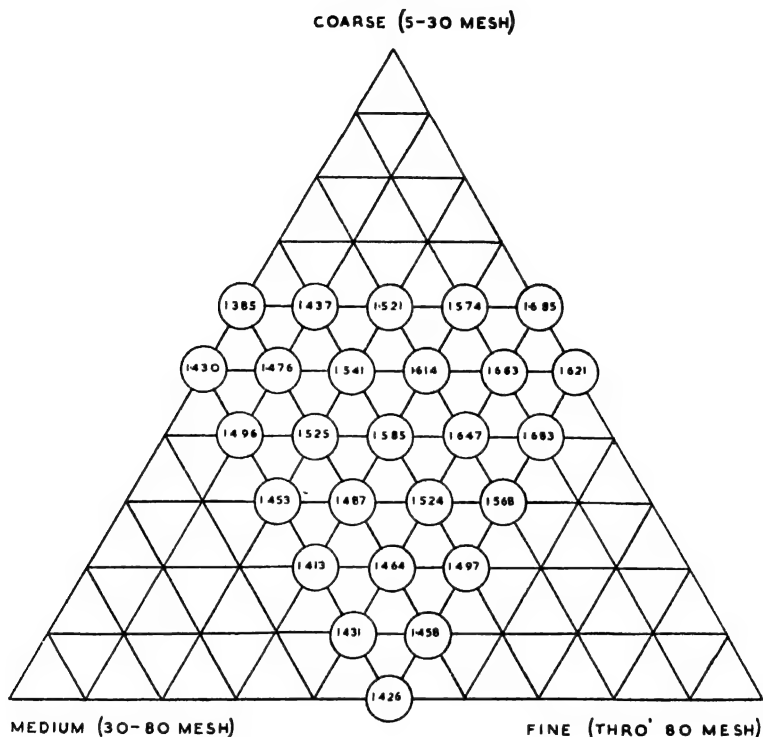


FIG. VII.10. THE RELATIONSHIP BETWEEN THE
APPARENT DENSITY AND THE GRADING OF FIRED MIXTURES OF SILICA ROCK
(after Hugill and Rees)

The proportions of each grade in a mixture may be indicated if each side of the triangle is sub-divided and three sets of parallel lines constructed by joining equivalent points. For example, the proportion of M at the apex is 1.0 but at points along the line GF it is zero. At any point on the line 0.6G—0.4M, the proportion of M is 0.4.

The point A corresponds to a material containing 48 per cent of size G, 16 per cent, of size F and 36 per cent of size M. A large number of samples may be plotted on such a diagram and the particle-size distribution of all of them can be clearly shown. Any three desired ranges of particle-sizes may be used and if a material contains a very small percentage of each of several sizes this may either be omitted or included with another size.

It was by means of such a diagram that Hugill and Rees¹ were able to forecast the most suitable blends of graded quartzite to give an optimum bulk density in the fired product. Their triangular diagram is shown in Fig. VII.10, and the figures within the circles indicate the bulk density of the fired material of that particular

¹ Hugill, W. and Rees, W. J., *Trans. Brit. Ceram. Soc.*, 30, 337, 1930.

blend. The best ratio of coarse:medium:fine particles was 45:10:45 which gave a maximum bulk density of 1.70.

Surface factors are based on the total surface area of all the particles in a given weight of material. So far as the ceramic industries are concerned the term was devised by W. Jackson to express the size distribution of particles by means of a single figure. He calculated the arithmetic average of each of the size-groups suggested by Seger (p. 375), assumed all the particles to be true spheres and deduced the average surface area of equal weights of grains of various sizes. From these figures, the *surface factor* was formed by multiplying the percentage weight of each grade by the average surface area of the grains included in that grade, adding the products so obtained and dividing the result by 100.

J. W. Mellor¹ showed that the true average diameter of a series of particles of different sizes is not the arithmetic mean but corresponds to

$$\sqrt[3]{\frac{D^4 - d^4}{4(D - d)}}$$

where D is the diameter of the largest and d that of the smallest particles in the group. Mellor assumed three groups of sizes:²

- (a) Particles below 0.010 mm.
- (b) Particles between 0.01 and 0.063 mm.
- (c) Particles between 0.063 and 0.107 mm.

and obtained three factors: (a) 359; (b) 53.9; and (c) 26.0 which, when multiplied by the respective weights of the different grades and the products added together, produces the surface factor.

No such surface factor can be fully accurate because it assumes that all the particles are truly spherical and are of the same weight—which is incorrect—and also because the conception of an 'average diameter' is inadequate. In spite of these disadvantages, such a surface factor is often convenient and is very useful in the works control of clays and other materials used in the manufacture of earthenware and porcelain.

The surface factor can also be calculated from a cumulative grain-size curve as illustrated in Fig. VII.5. Whittaker³ has shown that if the shape of particles is constant and is known—and hence the surface area of an individual grain of a certain size—the total surface area of a powder can be calculated by summing increments of weights corresponding to a small size-range on the cumulative curve.

Many other methods used to determine the particle size of powder can be applied to give a measure of the surface factor. Webb and Ratcliffe⁴ use a hydrometer technique which is of wide application in the routine control of slips and slurries. Moore⁵ has shown that the light absorption method (p. 386) gives satis-

¹ Mellor, J. W., *Trans. Eng. Ceram. Soc.*, 9, 94, 1910 and 29, 251, 1930.

² The extension to particles of smaller diameter than the above (200-mesh) greatly increases the error in the surface factor and is inadvisable though sometimes used.

³ Whittaker, H., *J. Amer. Ceram. Soc.*, 22, 16, 1939.

⁴ Webb, H. W. and Ratcliffe, S. W., *Trans. Brit. Ceram. Soc.*, 41, 51, 1942.

⁵ Moore, A. E., *Pottery Gazette*, 75, 849, 1950.

factory results for the surface factors of crushed flints. Leech, Ratcliffe and German¹ compared a light absorption method using a Spekker photometer, with the Rigden specific-surface apparatus (see p. 396) for determining surface factors of flint, colours and glazes, and showed that the results from both methods were closely related.

As the surface factor is directly related to the sizes of the various particles it affords a means of representing the size-distribution of these particles, but the result may be seriously affected by the fact that several materials each with widely differing proportions of particles of different sizes and densities (and therefore very different in their behaviour in a kiln) may all have the same surface factor. For this reason, this factor is chiefly of value in certain works where the kinds of materials used are few and where their composition and physical properties are reasonably constant. Thus, in a factory manufacturing fine earthenware, any change in the surface factor indicates a change in one or more of the ingredients used and so may act as a warning.

SPECIFIC SURFACE AREA

THE specific surface area of a ceramic material also depends on the sizes and shapes of the particles and if the *shape-factor*² is known, the average particle-size can be calculated.

The surface-area of a porous mass includes not only the exterior surface but the surfaces of all the pores and other open spaces between the particles. In practice it does not include the surfaces of any closed pores as these are inaccessible. For instance a cube of non-porous material with sides $1 \times 1 \times 1$ in. has a surface area of 6 sq. in. covering six faces each with an area of 1 sq. in. The surface area in a porous cube is very much greater, its amount depending on the sizes and shape of the units of which it is composed and the closeness of the packing.

The *specific surface-area* is the total surface area in square metres per gm. of material. A knowledge of the specific surface-area is often important because several properties of the material, including (i) the reaction-rate when heated, (ii) the crushing, tensile and transverse strengths of the finished articles, and (iii) the behaviour of a material with water, are all intimately related to it.

The specific surface area can be estimated in several ways, e.g.:

(i) By measuring the quantity of gas adsorbed and from that figure calculating the surface area. Methods in this group rely on the fact that molecules are adsorbed on the surface of particles by virtue of unsatisfied or polar valencies, so that if the adsorbed molecules are small, relative to the area of the surface of the individual particles, accurate determinations are possible. Gas adsorption methods, which are commonly used, measure not only the external area of crystals but also the area exposed along cracks and micropores within the crystal itself. The value thus derived may be one hundred times greater than that expected from purely geometrical considerations.

The measurement of specific surface area by gas adsorption methods was

¹ Leech, L. G., Ratcliffe, S. W. and German, W. L., *Trans. Brit. Ceram. Soc.*, **52**, 145, 1953.

² The *shape factor* is a figure used in place of the actual dimensions of the particles so as to yield an *equivalent diameter* (p. 381); it would be unity if the particles were true spheres.

developed largely by Emmett and Brunauer.¹ By the use of low temperature adsorption isotherms, the nature of the layers of gas molecules covering the surface of a particle can be predicted and provided that a monomolecular layer of molecules of known size and shape is adsorbed, the specific surface area of a powder can be accurately estimated. The gases nitrogen and argon are the most commonly-employed adsorption agents for clays and similar materials.

(ii) Other molecules or groups of molecules can be adsorbed on the surface of particles and may be used to measure the specific surface area. Stearic acid is such an example and Russell and Cochran² have shown that its long fibre-like molecules attach themselves to the surface of particles with the long axis of the molecule projecting outwards. As the packing of these fibres is constant, the amount of stearic acid adsorbed by a powder is in proportion to its surface area. Dye adsorption methods are based on the same principle.

In general, stearic acid or dye adsorption measurements give a lower value for the specific surface area of a material than gas adsorption methods, because the larger molecules do not penetrate as readily into crystal fissures and micropores as the smaller gaseous ones which are able to cover the internal surfaces more readily.

(iii) Schofield³ has described a method for the estimation of the surface area of clays by negative adsorption.

(iv) A method which does not involve wetting the substance is the gas-diffusion method devised by Lea and Nurse⁴ but which has been subsequently modified by Rigden⁵ to be capable of general application to ceramic bodies.

In principle, the method relates the rate of flow of air or other gas through a compacted powder or porous body to the surface area. The powder is lightly pressed on to a filter paper or perforated disc in a 1 in. diameter steel cylinder. A fixed volume of air is passed through the specimen and the time of flow is measured. Provided that conditions are standardised, the specific surface area (S) of the powder is related to the rate of flow by the expression:

$$S^2 = 5.65 \times 10^6 \left(\frac{\epsilon^3 T}{(1 - \epsilon)^2 \rho^2 d} \right)$$

where T is the time of flow in secs. of a fixed volume of air;

ρ is the specific gravity of the powder;

d is the depth of powder in cm.;

and ϵ is the fractional volume of voids in the compacted powder and is calculated from the equation:

$$\epsilon = 1 - \frac{W}{A \rho d}$$

where W is the weight of the powder (gm.) and A is the cross-sectional area of the cylindrical test sample.

¹ Emmett, P. H. and Brunauer, S., *Trans. Electchem. Soc.*, 71, 383, 1937.

² Russell, A. S. and Cochran, C. N., *Ind. Eng. Chem.*, 42, 1335, 1950.

³ Schofield, R. K., *Trans. Brit. Ceram. Soc.*, 48, 201, 1949.

⁴ Lea, F. M. and Nurse, R. W., *J. Soc. Chem. Ind.*, 58, 277, 1939.

⁵ Rigden, P. J., *ibid.*, 62, 1, 1943.

All methods so far described give little indication of the actual particle or crystallite size for to some extent they all measure the internal as well as the external surface area. The only techniques which are available to determine the true external area involve calculation from a sedimentation curve¹ or a tedious derivation of the value from a microscope count. In each case a shape factor correction has to be applied.

HOMOGENEITY

ALTHOUGH the raw material may be selected and prepared in such a way that the required texture should result, it is important that a homogeneous mixture of grains of all sizes should be secured. *Homogeneity* is a very desirable characteristic of a moulded shape but is often difficult to attain. If the initial mixing is not thorough, some parts of the fired body may have a different texture or even composition from others. The methods by which a homogeneous body may be produced include treading, wedging, pugging, tempering, rolling and blunging.

POROSITY

NO matter how carefully the various size grades of a raw material are mixed, it is virtually impossible to produce a body free from void space. All ceramic raw materials and products with the exception of glasses and similar bodies, are to some extent porous, therefore some fraction of the total volume is composed of air in the form of pores or voids.²

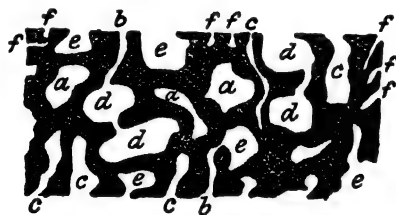


FIG. VII.11. VARIOUS KINDS OF PORES

The porosity of a material is defined as the total proportion of the air space contained between the solid particles of which the body is composed. Porosity should not be confused with permeability (p. 412) for the latter implies interconnected voids whilst the former embraces void space of all kinds.

According to E. W. Washburn³ there are six types of pores (Fig. VII.11): (a) closed or 'sealed' pores; (b) channel pores connecting separate pores; (c) blind-alley pores; (d) loop pores; (e) pocket pores—some with narrow necks; and (f) micropores, which are so small as not to be filled with water or other liquid in

¹ Whittaker, H., *J. Amer. Ceram. Soc.*, 22, 16, 1939. Allison, E. B. and Murray, P., *Trans. Brit. Ceram. Soc.*, 52, 204, 1953.

² Methods whereby the number and sizes of pores in ceramic materials can be measured have been described by L. Lecrivain (British Ceramic Society Meeting, April 1958).

³ Washburn, E. W., *J. Amer. Ceram. Soc.*, 4, 918, 1921.

any ordinary period of soaking. To these must be added the continuous pore which runs, perhaps with a complex path, from one external face of the body to another.

These different kinds of pores produce two sets of results when the porosity of a material is determined, viz. (a) the true porosity, and (b) the apparent porosity.

The *sealed or closed pores* are of two kinds: (i) those which are naturally closed; and (ii) those which were originally open, but have been closed by molten matter formed when the articles were heated. Those of the first class may contain air, water, sulphur dioxide or trioxide, carbon monoxide or dioxide, oxygen or hydrocarbons commonly termed gaseous inclusions.

When some clays are overheated the formation of bubbles of gas in them is greatly increased and the material swells. The bubbles each form a closed pore, and the whole mass, eventually has a vesicular structure and is frequently bloated and misshapen.

Sealed pores (with or without bloating) may also be formed by improper control of the kiln at a temperature of 700–950° C. They may be prevented by heating the articles more slowly and with more air at this range of temperature.

Pinholes and *blisters* may be regarded as forms of sealed pores. The first is usually due to the decomposition of calcium sulphate or other salt in the clay. Blisters may be due to a sudden overheating, or to mechanical defects in the shaping of the articles.

The *open pores* are those with an extremity on at least one surface and are the result of (a) the original packing of individual grains, (b) the escape of water during drying or of gases during firing, and (c) cracks and fissures which develop during drying and firing as a result of shrinkage (or expansion) of the material. They vary in size from that of a fine capillary to 1 mm. or more; the size depending largely on the coarseness and openness of the texture.

The **true porosity** is the ratio between the volume of all voids, both open and closed pores, and the total volume of the article.

The **apparent porosity** is defined as the ratio between the volume of water or liquid capable of being absorbed into it and the total volume of the article. Any closed pores, or for that matter, any open ones which are so fine that liquid cannot penetrate into them, will not be included as void space in determining the apparent porosity.

Both the true and the apparent porosity may be expressed as (a) percentage by weight, and (b) percentage by volume. The percentage of porosity by weight shows the weight of water or other liquid absorbed by 100 units of weight, whilst the percentage of porosity by volume is the volume of water absorbed in 100 volumes of the material or article. It is customary to use the latter and express the porosity by volume as this has the advantage of indicating the volume of the pores. The volume of articles of simple shape may be calculated from direct measurement of the dimensions, but where the shape is complex the volume must be determined by finding the difference between the weight when immersed in water and the weight in air. The expression 'porosity by weight' is unsatisfactory because all materials have not the same density (e.g. clay particles may have a density of 1.4 to 2.6), so that the 'porosity' of different samples cannot be compared accurately. The expression of porosity wholly in terms of volume is, therefore, the most satisfactory as well as being the most consistent.

The porosity of various materials may be influenced by some or all of the following: (a) the shape of the particles; (b) the size of the particles; (c) the grading of the particles; (d) the nature of the materials comprising the mixture; (e) the treatment to which the materials are subjected during manufacture; and (f) the relative position of the particles, i.e. whether they are closely compacted or lie loosely on one another.

Porosity can be reduced by careful grading although in general, the coarser the maximum size of the particles the less will be the porosity; in other words an ideally well-graded mixture of fine particles does not approach the theoretically-predicted minimum porosity figure as closely as a coarser mixture.

Angular grains when moulded under pressure give a lower porosity body than rounded ones, because interlocking takes place more readily. A mixture composed wholly of rounded grains cannot be compressed appreciably unless fracturing occurs, but a mixture of angular grains readily compacts under pressure to give a low porosity as shown in Table VII.IV.

TABLE VII—IV. EFFECT OF PRESSURE ON THE POROSITY OF CLAY

<i>Pressure (lb. per sq. in.)</i>	<i>Porosity (per cent)</i>	<i>Pressure (lb. per sq. in.)</i>	<i>Porosity (per cent)</i>
A 500	38.71	I 2500	26.87
B 750	34.73	J 2750	26.31
C 1000	32.59	K 3000	25.58
D 1250	30.83	L 3250	25.70
E 1500	30.65	M 3500	24.94
F 1750	29.83	N 3750	24.90
G 2000	28.83	O 4000	24.13
H 2250	27.47		

A fact which is often overlooked is that if the individual grains in a body are themselves porous, the body itself will have a porosity higher than that of a similarly graded mixture of non-porous particles. Thus, if the raw material is an aggregated clay, the porosity of the body will be related to the porosity of the grains. For this reason, a clay which contains a proportion of large-sized sand particles will have, all other things being equal, a lower porosity than a body composed of a purer clay.

The porosity is also greatly influenced by the methods used for moulding and the reactions which occur on firing. These will be discussed in more detail in the appropriate section (Chapter XII).

In some cases, a high porosity is desirable, particularly where a high thermal insulation is required. A large amount of air-space entrapped within the particles of the body presents the maximum resistance to the passage of heat particularly if the voids are discontinuous. Materials may be added to increase the porosity and the most usual example is carbonaceous material. When the mass is fired, the carbonaceous matter burns away, leaving corresponding pore-spaces, so that the porosity of the fired mass is roughly proportional to the volume of carbonaceous

matter added and is, in some cases, very high. The chief combustible materials added to clays, etc., to increase their porosity are hardwood sawdust, cork, seeds, naphthalene, and, occasionally, finely-ground coke. The maximum proportion of carbonaceous matter which can be added depends on the bonding power of the other ingredients. The porosity of a mass may also be increased by the addition of a porous material, such as grog, kieselguhr or vermiculite.

Gas bubbles may also be artificially introduced by adding finely-divided zinc powder to the raw material and then mixing dilute hydrochloric acid with the water added during moulding. Hydrogen gas is liberated which under certain conditions can be retained as gas bubbles. A froth-stabilising agent may also be added to a clay and bubbles introduced by agitating the plastic body.

One of the best-known ceramic thermal insulating materials is diatomaceous earth where a high porosity body is produced by a natural process. The origin and mode of formation of diatomaceous earth has been described in Chapter VI (p. 312) and as would be expected the skeleton structure is capable of entrapping large volumes of air. The porosity of such bodies is very high and the void space is mainly in the form of micro- or pocket pores. The result is that the heat transfer is low and at the same time there is not an excessive amount of gas permeability.

For most purposes, the size of pores should be less than 0.04 in. and in 'thin ware' it should not exceed 0.02 in.; otherwise, the strength of the mass is reduced and the heat insulation capacity is lowered largely as a result of the greater permeability.

The porosity of a raw material or ceramic body has a great influence on many properties. These include the property of absorption, spalling resistance, conductivity, mechanical and chemical erosion, refractoriness, strength and many others, all of which will be considered in other chapters.

The *porosity of raw clays* varies greatly according to their nature. Some plastic clays appear to be devoid of porosity, some fireclays have only about 3 per cent porosity, whilst some sandy loams have a porosity of 25 per cent or more. Occasionally clays which have a very low porosity in the damp state will absorb a large amount of water in excess of that previously present if they are first dried and then soaked in water. Use is made of this property when it is desired to soak clays in pits prior to converting them into a highly plastic paste of suitable consistency for moulding.

The amount of water absorbed by dry clay is often considerable, in some cases being as much as 80 per cent by weight. This absorptive power is due mainly to the colloids present in the clay, but the rapidity and ease with which it takes place is a result of the capillary structure of the clay particles. In any case, the total absorptive power of a plastic clay is not strictly proportional to the volume of the pores, as more water appears to be absorbed than is required to fill the pores and the absorption is also accompanied by a swelling of the material similar to but far less than, that of glue.

THE MEASUREMENT OF POROSITY

As explained previously there is a distinction between the true and apparent porosity, but in most cases the term 'porosity' is applied to the apparent porosity as estimated from the amount of water or other suitable fluid absorbed by a given

weight or volume of the sample. Hence the *absorption* or *apparent porosity* is a measure of the unsealed pores.

The usual way of carrying out the determination¹ is to take a conveniently-sized test piece, if possible a 2 in. cube, which is weighed (W_1) after being thoroughly dried. To ensure that liquid completely fills all unsealed pores the sample should be placed in a vacuum vessel and evacuated. Without releasing the pressure, the immersion liquid must then be introduced to such a level that the piece is entirely covered. The saturated sample may then be weighed in air (W_2) by suspending it from a thread attached to the arm of the balance; and finally the weight of the sample when immersed in water (W_3) has to be measured.

The weight of liquid absorbed is given by $W_2 - W_1$ gm. and provided that water (density = 1) is used for immersion this figure is also the volume of the open pore spaces in cubic centimetres. The total volume of the test piece is $W_2 - W_3$, i.e. the weight 'lost' on immersion in water, so the percentage apparent porosity by volume (P) is given by the equation

$$P = \frac{W_2 - W_1}{W_2 - W_3} \rho$$

(where ρ is the density of the liquid which will be 1 if water is used).

If a vacuum equipment is not available an alternative technique capable of giving results comparable in accuracy has been described by Cross and Young.² The method is to immerse the specimen heated to just above boiling point in boiling liquid. As cooling proceeds the air space is completely filled and the procedure is then as above.

An accurate method which is suitable for small test specimens and those which break up on immersion in liquid is shown in Fig. VII.12.

The specimen holder (H) is usually cylindrical, although any size may be selected depending on the shape and dimensions of the samples being tested. A glass plate closes the lower end of the holder, the seal being made by vaseline or vacuum grease.

To calibrate the apparatus before use the glass plate is securely fixed to the specimen holder and tap T_1 closed to isolate the round-bottom flask (F) which should be of comparable volume to the specimen holder. The assembly is evacuated by turning tap T_2 to the appropriate position—the pressure can be observed on the manometer (M). When evacuation is complete, tap T_2 is closed, tap T_1 opened and the pressure (P_1) calculated from the difference in levels in the two manometer arms. The reading of the scale on the specimen-holder side of the manometer should be carefully recorded (S). The assembly may then be restored to atmospheric pressure by adjustment of tap T_2 .

A bar of metal of known volume is then placed in the specimen holder and the test repeated, but after tap T_1 has been opened the level of mercury in the left-hand manometer arm must be adjusted to S by running in mercury from the reservoir (R)—this is to ensure that the volume in the assembly is maintained constant. The pressure is again measured (P_2).

¹ See *British Standard B.S.S.*, No. 1902, 1952.

² Cross, A. H. B. and Young, P. F., *Trans. Brit. Ceram. Soc.*, 47, 121, 1948.

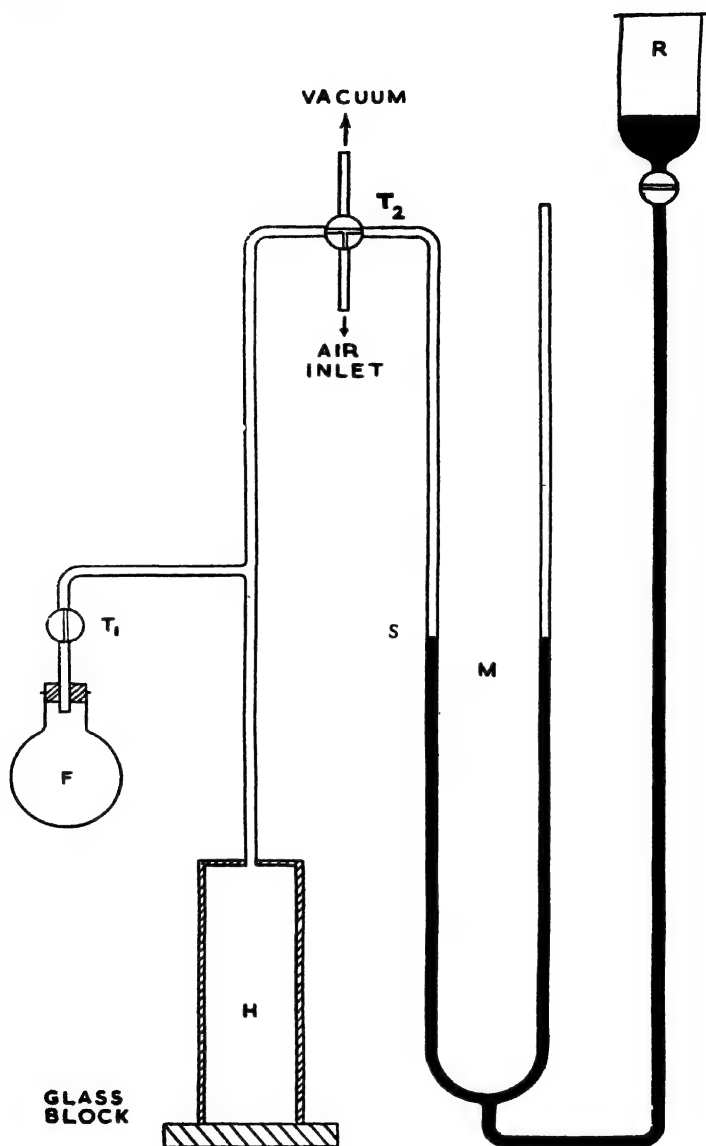


FIG. VII.12. AN AIR POROSIMETER

If V_1 is the volume of the assembly comprising the specimen holder (H), round-bottomed flask (F) and connecting tubing to S; and V_2 is the volume of the metal bar, from Boyle's law:

$$P_1 V_1 = P_2 (V_1 - V_2)$$

hence V_1 can be calculated.

When measuring the porosity of a sample the same procedure is repeated with a specimen, the bulk volume V_t of which has been determined by means of the mercury volumeter (p. 408). Once again, after opening tap T_1 , the level of mercury in the left-hand manometer tube must be adjusted to S before the pressure (P_3) is determined. If V_3 is the volume of the sample, then as before:

$$P_1 V_1 = P_3 (V_1 - V_3)$$

hence V_3 can be calculated.

The porosity by volume is

$$\frac{V_t - V_3}{V_t}$$

The true porosity cannot be determined directly as it not only includes the pores which are open to a surface but also all sealed pores to which there is no direct access without destroying the mass by grinding to a powder. The volume of sealed pores can be derived only after first determining the true specific gravity and bulk density.

TRUE SPECIFIC GRAVITY

THE definition of the true specific gravity of a substance is the ratio between its weight and that of an equal volume of water. The term *density* is now considered to be synonymous with specific gravity although its use may lead to confusion, particularly when applied to ceramic bodies which are often porous. The true specific gravity of a *crystal* may be expressed in terms of the dimensions of the atoms or ions which make up the lattice. The weight of the atoms in a crystal and the way in which they are arranged determine the specific gravity and the introduction or removal of atoms or a rearrangement within the lattice are the only agencies which can alter its value. For example, rock-salt (NaCl) crystallises in the cubic system where the unit-cell dimension is 5.628 Å and there are four molecules of NaCl in each unit cell. The four molecules of NaCl imply four atoms each of sodium and chlorine, the atomic weights of which are, respectively, 22.997 and 35.457. The weight of each atom is the atomic weight divided by Avogadro's Number (6.02×10^{23}) (see p. 63).

Therefore, the weight of the atoms in a unit cell is

$$\frac{4 \times 22.997}{6.02 \times 10^{23}} + \frac{4 \times 35.457}{6.02 \times 10^{23}} = \frac{233.816}{6.02 \times 10^{23}} \text{ gms.}$$

This weight is contained within the boundaries of the cubic unit cell of side 5.628 Å (where $1 \text{ Å} \equiv 10^{-8} \text{ cm.}$). The total volume occupied by the atoms is therefore $(5.628 \times 10^{-8})^3$ cubic centimetres.

The specific gravity of rock-salt is, therefore,

$$\frac{\text{weight}}{\text{volume}} = \frac{233.816 \times 10^{24}}{6.02 \times (5.628)^3 \times 10^{23}} = 2.179$$

Replacement of sodium ions by potassium gives the mineral sylvine, KCl, which is also cubic with a unit cell length of 6.277 Å. The atomic weight of potassium is 39.096 and calculating as before

$$\text{Specific Gravity} = \frac{\text{weight}}{\text{volume}} = \frac{4 \cdot (39.096 + 35.457) 10^{24}}{6.02 \cdot (6.277)^3 \cdot 10^{23}} = 2.002$$

The determination of the true specific gravity of all perfect crystals can be calculated in this way provided the dimensions of the unit cell and the number of molecules in it are known. These data for most ceramic minerals are given in Chapters III and IV and in the Appendix.

The simple examples considered above indicate how both the absolute weight and the size of atoms contribute to the specific gravity of a compound. All other things being equal it is obvious that atoms where the ratio of atomic weight to atomic size is large will form compounds of high specific gravity.

Another factor which influences the true specific gravity of crystals is the way in which the individual atoms are arranged. Thus quartz, cristobalite and tridymite are all pure SiO_2 , yet the specific gravities are respectively 2.65, 2.32 and 2.28. The individual atoms in the crystal lattices of each mineral are arranged differently so that the packing in quartz is closer than that in cristobalite which in turn is not as open as that of tridymite. For more details see Chapter III (p. 162). The true specific gravity is difficult to determine accurately for crystals are rarely, if ever, perfect and are liable to contain micro-pores, inclusion and other imperfections. In most cases, the errors which arise as a result of crystal flaws are not serious except when values correct to several places of decimals are required.

A ceramic body or raw material may be made up of many crystals and perhaps colloidal or glassy material; the specific gravity is the resultant of the various components. It may be determined by several methods depending on whether the material is a solid mass, a powder or a liquid.

The true specific gravity of a non-porous solid may be determined by:

(a) Weighing a piece of the solid and then suspending it in water and re-weighing it. The specific gravity is found by dividing the weight of the material by its loss of weight in water, i.e. specific gravity = $W_s \div (W_s - W_w)$ where the weight of the dry sample = W_s and the weight of the sample immersed in water = W_w .

(b) Weighing a piece of the material, measuring its volume in a volumeter and dividing the weight (in grams) by the volume (in c.c.).

The specific gravity of a porous solid may be determined by:

(i) By method (a) above, or

(ii) By method (b) above, but in both cases using the volume of the sample, after deducting the volume of the pores which can be filled by saturating the sample

with water as described on p. 401. Neither of these methods will be accurate if the material contains any fine or sealed pores.

(iii) Grinding the material to a fine powder, the individual grains of which are too small to contain any pores and determining the specific gravity in the manner described below.

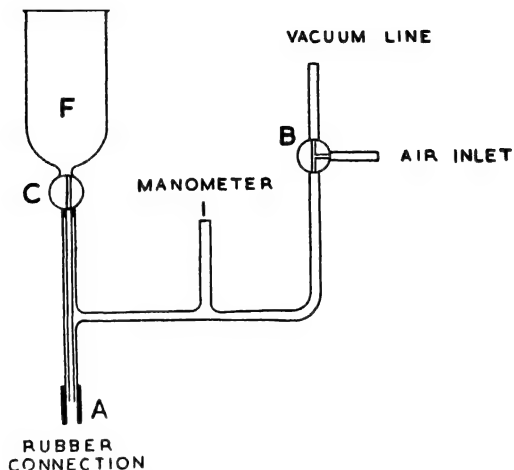


FIG. VII.13. AN APPARATUS FOR FILLING SPECIFIC GRAVITY BOTTLES WITH DISTILLED WATER UNDER VACUUM

Vitrified materials are anomalous, because they may appear to be non-porous and yet may contain many sealed pores. Hence, they should be ground to a very fine powder before their true specific gravity is determined, as, unless the sealed pores are broken open, low results will be obtained.

The **true specific gravity of a powder** may be determined by means of a specific gravity bottle, pycnometer or a Rees-Hugill flask.¹ The bottle and stopper are cleaned, dried and weighed ($= P$); a sufficient quantity of the dry powder (crushed to pass a 120 B.S.I. sieve) to half fill the bottle is placed in it and the bottle is again weighed ($= W_1$); the weight of powder is thus given by $(W_1 - P)$. The bottle must now be filled with water and freed from all air. Satisfactory results can be ensured only by evacuating the air and then filling under vacuum with distilled water, which has been boiled to eliminate dissolved air bubbles and then cooled in the absence of air. A suitable apparatus is shown in Fig. VII.13. The specific gravity bottle without stopper is attached by a small piece of rubber tubing to A, and is evacuated by opening tap B which leads to a vacuum pump. When the pressure indicated by the manometer has become constant, distilled water is added from the funnel (F) by opening tap C. The system may be returned to normal pressure by opening tap B to air when the filling has been completed.

As the specific gravity of water varies with temperature, the filled bottle which must now be stoppered should be placed in a thermostat until its temperature is

¹ See *British Standard B.S.S.*, No. 1902, 1952, p. 28.

constant. Excess water overflowing through the stopper can be removed with blotting paper and the bottle and contents weighed (W_2). The bottle is then emptied, cleaned, refilled with distilled water and again brought to constant temperature prior to weighing again (W_3). The volume of the bottle is $(W_3 - P)/\rho$ where ρ is the density of water or other fluid used at the temperature of the test.

The true specific gravity is given by the formula

$$\text{S.G.} = \frac{(W_1 - P)}{(W_3 - P)\rho - (W_2 - W_1)}$$

The results of duplicate determinations should agree to 0.005.

If the solid is affected or changed by immersion in water, some inert liquid such as xylene must be employed. The same formula for determining the specific gravity is used but the correct value for ρ (the density of the liquid used) must be substituted.

Typical figures for the true specific gravities of clay minerals are:

Kaolinite	2.60–2.68
Halloysite ($2\text{H}_2\text{O}$ form)	2.5–2.6
Halloysite ($4\text{H}_2\text{O}$ form)	2.0–2.2
Montmorillonite	2.3–2.8 ¹
Illite	2.6–3.2 ²

According to R. E. Grim³ it is particularly difficult to obtain really accurate figures for the true density or true specific gravity of montmorillonite, halloysite and illite clays because they contain a variable amount of water as an integral part of their structure. Moreover, as isomorphous substitution is common, the density of different samples varies greatly, even in the same locality, and no single figure is truly typical. Samples with less than 1 per cent of moisture range in density from 2.0–2.8—depending partly on the iron content in samples with a density greater than 2.5.

The specific gravities of other minerals in ceramic materials are characteristic and their determination may be informative. The raw materials used in the preparation of *basic* refractory materials have high values and can thereby be distinguished. The specific gravities of many of the minerals are to be found in the appendix.

The **specific gravity of slips or suspensions** offers an important means of control in the obtaining of uniform results in slip-casting, engobing or slip-coating and glazing. A glazing-slip of too low a specific gravity will form too thin a coating on the ware, whilst one which is too high will cause defects by forming too thick a coating.

When the quality of a suspension is being controlled by specific gravity methods, care must be taken to ensure that the components are not changed in amount or obtained from a different source. Thus variations in the specific gravity of a flint for use in fine earthenware or china ware may cause the weight of flint in a slip to change by as much as 13 per cent and a potter who is unaware of this may unwittingly produce badly crazed ware.

¹ According to water—and iron—content.

² Some samples are as low as 1.5—due to moisture.

³ Grim, R. E., *Clay Mineralogy* (McGraw-Hill Publishing Co. Ltd., London, 1953).

The **true specific gravity of a liquid** may be determined as follows:

(a) By immersing a suitable hydrometer in the liquid and noting the figure on the stem which coincides with the surface of the liquid; such an instrument is frequently used in the control of body-slips and glazes and to determine the weight of dry material in them; or

(b) By means of a Westphal balance in which a glass plummet is immersed in the liquid and weighed in that position. Special weights are used which enable the specific gravity to be read off directly without calculation; or

(c) By using a specific gravity bottle or pycnometer. The weight of liquid to fill the bottle is compared with the weight of an equivalent volume of water. The specific gravity of the liquid is given by the expression:

$$\text{S.G.} = \frac{W_l - P}{(W_w - P)\rho}$$

where P is the weight of the bottle;

W_l is the weight of bottle and liquid;

W_w is the weight of bottle and water;

and ρ is the specific gravity of water.

Normally the specific gravity of water (ρ) may be taken as 1 but for accurate work a correction to allow for the temperature of test must be used.

Specific gravity of water	10° C.	20° C.	30° C.
	0.9997	0.9982	0.9956

A rapid method of assessing the **weight of solid matter in a slip** is to determine the specific gravity in ounces per pint and then apply the formula

$$\text{Weight of solid matter in a pint of slip} = (D - 20) \frac{G}{G - 1}$$

where G is the true specific gravity of the solid matter and D is the specific gravity of slip in ounces per pint.

If G is 2.6, which is the approximate value for many ceramic materials the formula above reduces to

$$\text{Concentration of slip (ounces per pint)} = (D - 20) \times 1.625$$

A rough means of measuring the *specific gravity* (D) of a slip is to fill a weighed or counterpoised cylindrical vessel with the slip and then with water. The weight of slip (in ounces) divided by the weight of water (in ounces) gives the specific gravity.

APPARENT SPECIFIC GRAVITY

THE term **apparent specific gravity** or **bulk specific gravity** is used to indicate the relation between the weight of a mass of material as a whole and that of a volume of water equal to the total volume of the mass less the volume which can be filled with water (i.e. the volume of the solid material *plus* the sealed pores).

Many ceramic materials—especially when fired—contain 'sealed pores' into which water cannot penetrate. These reduce the apparent specific gravity of the

material, so that the true specific gravity cannot always be found by subtracting the volume of the pores (as ascertained from the volume of water absorbed by the material) from the total volume of the mass; the result so obtained is not necessarily the volume of the solid matter, but the volume of the solid matter plus that of the sealed pores. When a material is ground to a fine powder, however, the sealed pores are destroyed and the sum of the volume of the individual grains forming the powder is the true volume of the solid matter, and from this the *true specific gravity* is obtained. The difference between the true and apparent specific gravities depends on the nature of the material examined.

APPARENT DENSITY OR BULK DENSITY

WITH the exception of air-free glasses or single crystals, ceramic bodies are invariably porous to some extent. Air or gases are entrapped between and within the grains of the body or they may fill pores within the structure with the result that the external volume of the body is much greater than the actual volume of the material of which it is composed. The body has thus an *apparent density* which is simply the ratio of the total weight to the external volume.¹ The smaller the space into which the solid matter can be packed the greater will be its apparent density, and the closer the approach to the true specific gravity, so that the shape and size of the grains and the grading of the mixture greatly influence this figure. If a material has a porous texture it will necessarily have a low apparent density, because a considerable portion of the volume of the mass will be occupied by the light-weighting air in the pores. On the other hand, a material of a glassy or vitrified nature will have a similar apparent density and true specific gravity, because there are few pores in it.

The true specific gravity of the solid portion of the material will affect the apparent density, because the higher the true specific gravity, the greater (other things being equal) will be the apparent density. Thus, a piece of silicon carbide having the same proportionate volume of pores as a piece of fireclay brick will have a greater density because, whilst both pieces have the same total volume and the same volume of solid grains, the silicon carbide has a true specific gravity of 3.17–3.21, whilst the fireclay brick has a true specific gravity of only 2.6.

Apparent density is thus a function of the true porosity and true specific gravity, and factors which influence those properties will also affect the apparent density. In calculating stress factors in brickwork construction, the apparent density is an important figure.

It may be measured quite simply in several ways:

(a) A first indication of the value can be obtained by calculating the volume of a symmetrical shape from the external dimensions and dividing into the total weight.

(b) A more accurate method is to use a mercury volumeter which is illustrated in Fig. VII.14. The sample container (A) is usually of cylindrical shape and is capable of being split to insert the specimen. The external volume is given by the

¹ If the bulk density is expressed in grams per c.c. the bulk specific gravity will be identical, as water has a specific gravity of 1.0, 1 c.c. of water weighing 1 gm. If the bulk density is expressed in 'lb. per cu. ft.' the corresponding bulk specific gravity can be found by dividing by 62.3 which is the weight (in lbs.) of 1 cu. ft. of water.

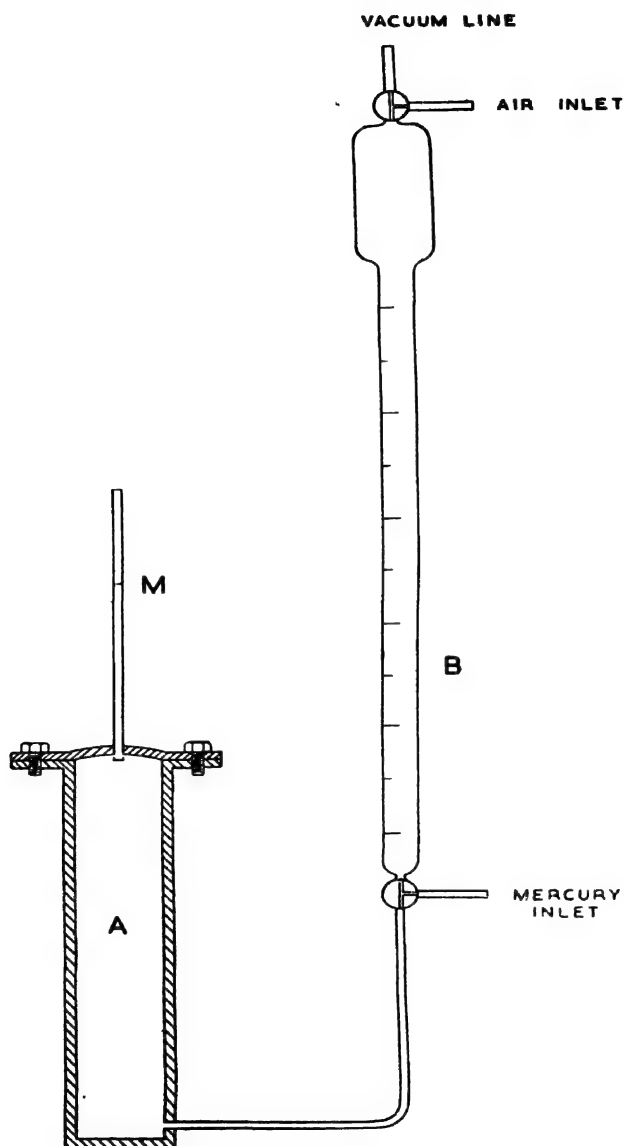


FIG. VII.14. A MERCURY VOLUMETER

difference in mercury levels in the burette (B) on filling to a mark (M) firstly with and secondly without the specimen in place. If the sample is exceptionally porous, mercury may enter some of the pores; in such cases, it is advisable to coat the specimen with a thin film of paraffin wax before testing.

(c) The apparent density can be determined along with the apparent porosity by the liquid impregnation method described on p. 401, and by its use the apparent specific gravity, true porosity and percentage of sealed pores may also be calculated.

The specimen is weighed dry (W_1), impregnated with water or other liquid, weighed again in air (W_2) and finally suspended in water (W_3).

The properties to be measured are related to three important volumes which may be expressed as:

V_m = volume of solid material

V_o = volume of open pores

V_c = volume of closed pores

From the weights above

(a) The total external or bulk volume $V_t = V_m + V_o + V_c = W_2 - W_3$.

(b) The volume of open pores $V_o = W_2 - W_1$ (provided water is the immersion liquid used).

The *percentage apparent porosity* (P_A)

$$= \frac{V_o}{V_t} = \frac{W_2 - W_1}{W_2 - W_3} \times 100 \text{ per cent} \quad . \quad . \quad (1)$$

The *apparent density* or *bulk density* (D_A)

$$= \frac{W_1}{V_t} = \frac{W_1}{W_2 - W_3} \quad . \quad . \quad (2)$$

The *apparent specific gravity* (S_A)

$$\begin{aligned} &= \frac{W_1}{V_m + V_c} = \frac{W_1}{V_t - V_o} = \frac{W_1}{(W_2 - W_3) - (W_2 - W_1)} \\ &= \frac{W_1}{W_1 - W_3} \quad . \quad . \quad . \quad . \quad (3) \end{aligned}$$

$$\text{The true specific gravity } (S_T) = \frac{W_1}{V_m} \quad . \quad . \quad . \quad . \quad (4)$$

(cannot be determined except by the powder method p. 405).

$$\text{The true porosity } (P_T) = \frac{V_o + V_c}{V_t} = \frac{V_t - V_m}{V_t} = 1 - \frac{V_m}{V_t} \quad . \quad . \quad (5)$$

From equations 2 and 4:

$$\frac{\text{apparent density } (D_A)}{\text{true specific gravity } (S_T)} = \frac{W_1/V_t}{W_1/V_m} = \frac{V_m}{V_t} \quad . \quad (6)$$

Substituting this value in equation 5:

$$P_T = 1 - \frac{D_A}{S_T} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The percentage true porosity is given by multiplying by 100. Therefore the true porosity can be derived if the values of the apparent density and true specific gravity are known.

The *percentage of closed pores* (V_c) is

$$P_c = \frac{V_c}{V_t} = \frac{V_t - (V_m + V_o)}{V_t} = 1 - \frac{V_m}{V_t} - \frac{V_o}{V_t}$$

substituting values from equations 1 and 6

$$P_c = 1 - \frac{D_A}{S_T} - P_A \quad \left(\text{but } 1 - \frac{D_A}{S_T} = P_T \right) \quad (\text{equation 7})$$

Therefore

$$P_c = P_T - P_A \quad . \quad . \quad . \quad . \quad . \quad (8)$$

i.e. the percentage of closed pores is equal to the difference between the percentage true and apparent porosities.

The number of closed pores in a ceramic body depends on many factors, but is mainly the result of vitrification having taken place and the liquid produced effectively seals off air and gas bubbles.

To eliminate much of the tedium involved in calculating the various values when many samples have to be analysed, Lakin¹ and Cross and Young² have devised rapid calculator charts and nomograms which enable the results to be read off directly once the weighings have been completed.

The values of the true specific gravity, apparent density, and apparent porosity for some raw materials are shown in Table VII.V. The figures are only approximate and some samples give very different values when they are collected from other localities. The values for fired products are given in Chapter XII (p. 736).

TABLE VII—V. PHYSICAL CHARACTERISTICS OF
CERAMIC MATERIALS

Type	True Specific Gravity	Apparent Density	Apparent Porosity (per cent)
<i>Raw materials</i>			
Raw china clay	2.60–2.68	1.10–1.25	50–55
Plastic ball clay	2.40–2.80	1.40–1.60	35–45
Fireclay	2.60–2.70	1.70–2.10	30–35
Brick clay	2.30–2.80	1.60–2.10	20–40
Quartzite	2.65	2.60–2.65	1–2
Flint	2.61–2.63	2.52–2.6	—
Raw kyanite	3.5–3.7	3.5–3.7	1
Dolomite	2.85–2.90	2.75	—
Chrome ore	3.8–4.6	4.30 (av.)	—
Magnesite ($MgCO_3$)	2.9–3.1	2.90	—

¹ Lakin, J. R., *Trans. Brit. Ceram. Soc.*, 50, 208, 1951.

² Cross, A. H. B. and Young, P. F., *Trans. Brit. Ceram. Soc.*, 49, 191, 1950.

PERMEABILITY

PERMEABILITY may be defined as the readiness with which a substance permits a fluid to flow through it and is measured by the rate at which water, air, or other gas flows through a mass of unit area and unit thickness at unit pressure. The permeability is due to the pores, voids, cracks or fissures which either run completely through the material or are connected with others to form a series which extends through it. The fluid which fills sealed or closed pores without passing through them is not included in measurements of permeability.

The permeability (P) is most conveniently expressed by the use of an equation in which

$$P = \frac{\text{volume of air or water passed (c.c.)} \times \text{thickness of specimen (cm.)}}{\text{area of cross-section of specimen (cm.}^2\text{)} \times \text{pressure (cm. of water)} \times \text{time of flow (sec.)}}$$

As pressure is necessary to cause the flow, it is necessary to specify the pressure or head of the fluid. Water is occasionally employed, but air or other gas, being much more mobile, gives more accurate results.

The permeability of a ceramic article made by mechanical pressure is usually greatest in a direction at right angles to that at which the pressure was applied. This is not so noticeable in articles made by hand. In those made by extrusion (e.g. wire-cut bricks) the permeability is usually greatest in the direction in which the pressure was applied during manufacture.

The maximum permeability in one direction is possessed by a structure composed of a large number of minute (capillary) tubes, arranged parallel to each other. Apart from the resistance caused by the surface tension of the walls of the tubes such a 'honeycomb structure' would be completely permeable. In the ceramic industries no materials are known which possess this structure, so that the permeability is usually due either to fissures or cracks in the materials or to numerous pores being connected and so forming irregular channels.

To be wholly impermeable, a material must be very compact and close in texture, at any rate on its exposed surface, and for this reason such surfaces are often covered with a glaze. Where a large article has to be repeatedly heated and cooled, a wholly dense material is undesirable on account of the low resistance to temperature changes of most ceramic materials of this nature. Under such conditions the 'body' of the article is usually made of a porous, coarse-grained material, the required impermeability being obtained by glazing, either the interior or exterior surface.

In paving bricks and tiles, porcelain and some forms of stoneware, the requisite impermeability is produced by the interaction of fluxes and the material of which the goods are made, with the result that the greater part of the pores present in the early stages of firing are later filled with a glassy mass of fused silicates which renders the article impermeable. The production of impermeable articles is costly and in many cases both unnecessary and undesirable, but in others it is essential.

The permeability of a mass of raw clay depends on its plasticity and moistness. If a clay is quite dry its plasticity is dormant and it will be readily permeable to water, yet the same clay when wetted and its plasticity made 'active' will be impermeable to water. This is attributed to the fineness of the grains and the power with which they retain the water in contact with them. The added water does move

through the interstices under pressure, but the motion is so slow that it may be non-apparent.

The permeability of an article depends on (*a*) its thickness; (*b*) the kind, number, distribution and sizes of the pores; (*c*) the presence or absence of cracks, fissures and holes; (*d*) the presence or absence of a superficial glaze or slag; (*e*) the difference in pressure on opposite sides; (*f*) the nature of the penetrating fluid; (*g*) the difference in the temperature of opposite sides of the article; and (*h*) the duration of the test.

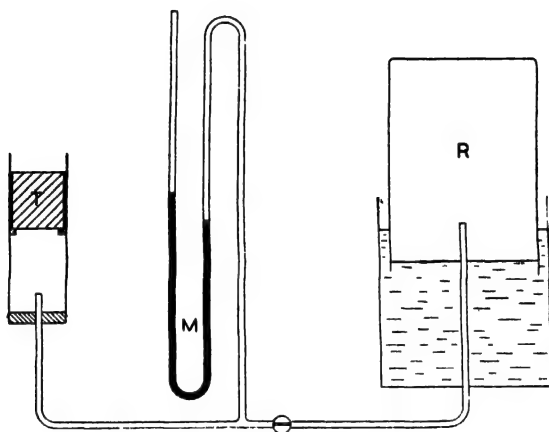


FIG. VII.15. AN APPARATUS FOR MEASURING THE PERMEABILITY OF CERAMIC MATERIALS

In several of these respects permeability differs greatly from porosity, for whereas the latter is a measure of the total volume of the pores, the permeability depends on the extent to which they penetrate through the mass. A glazed brick may have a high porosity, but it should, when in use, be impermeable so long as the glaze is undamaged. In other words, permeability depends chiefly upon the number of channels or connected pores which enable the permeating fluid to pass through from one side of the article or test-piece to the other. Pores which are closed at one end, or do not penetrate far into the mass, take no part in producing a permeable mass; a single small crack penetrating right through the mass may increase the permeability more than will a thousand short or disconnected pores. In short, whilst highly porous articles are often highly permeable, there is no definite relation between the porosity and permeability of a material.

The Permeability of ceramic materials is usually determined on a cylindrical sample about 3 in. long and 2 in. diameter (Fig. VII.15).¹

The test-piece (T) is placed in an iron vessel sealed at its lower end with a rubber ring or modelling clay and the gap between it and the walls of the vessel filled

¹ British Standard No. 1902: 1952 contains a detailed description of the British Standard method: it permits either a square or cylindrical testpiece and specifies the size as 'at least 7 cm. high and at least 25 sq. cm. cross-section'.

with mercury. Air is then forced through the test-piece at a steady rate and at a constant pressure not exceeding 20 cm. water-gauge for a measured period of time and the volume of air used is measured (usually by the amount of water used to displace it from an air-holder (R) which forms part of the apparatus). Frequent readings of the manometer (M) indicating the water-gauge pressure of the air should be noted and the average used.

The permeability (P) is measured in terms of the volume (c.c.) of air¹ passed vertically through the test-piece in unit time and reduced to an imaginary test-piece of unit cross-section and stated height.

Thus, if P = permeability, V = volume of air (c.c.) passed through the test-piece in t seconds under a pressure of p cm. of water, A is the cross-sectional area of the test-piece in sq. cm. and H is the height of the test-piece in cm.

$$P = \frac{V \times H}{t \times A \times p}$$

A slightly different procedure is described in British Standard 1069 (1953) which includes the determination of the maximum pore-diameter, the uniformity of pore-diameter and the relationship between pore-diameter and permeability.

The permeability of loose powders is determined in a similar manner using a circular metal box with an internal diameter not less than 5 cm. in which the bottom is formed of wire gauze. On this is laid a sheet of thin filter paper to prevent the powder from falling through. The box is then filled with the powder to a suitable height (e.g. 2.5 cm.) on which is a second sheet of filter paper. This arrangement is used instead of the test-piece described above.

When the penetrability to water is to be determined, a simpler arrangement can be used and the water allowed to travel downward whereas the air usually rises through the test-piece (see *British Standard Specification*, No. 402 : 1945).

As the permeability often varies greatly in different parts of the same sample, on account of fissures and small holes and lack of homogeneity (p. 397), it is often difficult to obtain satisfactory results unless all the particles are approximately spherical and as nearly as practicable of the same size, as in some ceramic filters.

PENETRABILITY

FOR many purposes the porosity and permeability values are not sufficient to describe the behaviour of a body to the passage of liquid. This is particularly true when estimating the amount of slag penetration in a refractory brick, but it also applies to the water absorption properties of other bodies, e.g. the manner in which a liquid may be drawn into the pores of a body by capillary action. Although penetrability is specifically a physical phenomenon, it may be impossible and even undesirable to dissociate it from the chemical action which occurs between the body and liquid.

¹ Helium is also used particularly for glasses and porcelains (see F. J. Norton, *J. Amer. Cer. Soc.*, 30 (3), 90, 1953).

The amount of liquid absorbed by capillary action depends on the nature and viscosity of the liquid, its wetting action on the solid, the surface tension, the temperature, the time of contact and the position of the surface of the articles with respect to that of the liquid level.

All else being equal, the velocity at which a liquid penetrates a porous mass is approximately proportional to the cube of the radii of the pores and inversely related to the height to which it ascends. Hence, a coarse-grained brick is more penetrable to water than a fine-grained one.

CHAPTER VIII

THE INFLUENCE OF WATER IN CERAMIC SYSTEMS

THE role of water in ceramics is of the greatest importance. Most raw materials are sedimentary in character and have therefore been laid down in a watery medium; furthermore, many of the principal mineral types are secondary products, resulting from the breakdown of primary rocks through the agency of water and, in addition, water is added to most ceramic bodies to facilitate shaping during manufacture. Hence the physical processes which are involved in the conversion of a rock-like body to a slip or plastic paste must be carefully studied.

Although the properties of all ceramic materials are affected to some extent by the addition of water, clays are by far the most susceptible and for this reason, the present Chapter deals principally with clay/water relationships.

If a piece of clay is placed in a large volume of water, the latter will gradually permeate the former, loosening and separating the particles and causing a *swelling* of the mass, until it *slakes*, or falls to pieces. The disintegration may be hastened by grinding or stirring the clay and water and, if they are sufficiently well mixed together, a *slip* or *slurry* is obtained. If the amount of water used is only about one-fifth of the weight of the clay and the mixing is sufficiently thorough, a plastic paste is produced. This paste can be hardened by drying, or it can be converted into a slip by mixing it with a further quantity of water.

At first sight, the action of water on clay appears to be simple; if only a little water is present, the particles of clay adhere well together and the solid mass increases in softness—roughly in proportion to the water present. If a large excess of water is added, the particles of clay are separated from each other and again their behaviour appears to be easily understood but, on investigating the matter still further, it is found that clays are the only natural minerals which possess, in so high a degree, the properties of *plasticity*. A still further investigation will show that clays have many other unusual physical properties; some of which are possessed by complex organic substances such as gums, resins, glue, etc., but clays differ from them in not being completely consumed when heated in a current of air. Plastic materials of an organic nature are wholly destroyed by heat, but clays are converted thereby into hard, stone-like bodies.

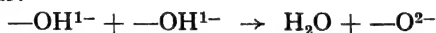
When clays are mixed with water, the properties of the resulting suspension are those of a true colloid and the study of clays from the standpoint of colloid chemistry has led to a more complete knowledge of their behaviour.

Before considering the concept of a clay as a colloid, it is as well to look more closely into the ways in which water may be present in ceramic materials, particularly clays, and some of the physical changes which are the result of water addition.

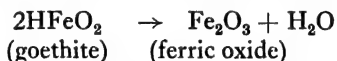
FORMS OF WATER IN CLAYS, ETC.

WATER is known to exist in many forms in clays and similar materials, but the boundaries of each form are not clearly defined and there is considerable overlapping. The principal types are as follows:

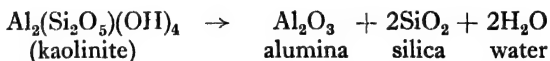
1. **Combined water** is present in clays and many secondary alteration products. The usual form is as hydroxyl groupings (cf. the structure of clays, Chapter III), but isolated water molecules are occasionally present. Combined water is often termed *water of constitution*, and sometimes *water of crystallisation*, although the latter is incorrect in some instances. The combined water in clays and related minerals is a definite part of the crystal lattice and is only liberated at a comparatively high temperature when the mineral decomposes. If hydroxyl units are lost, the reaction may be represented as:



Hydrogen ions may combine with oxygen or hydroxyl units to generate water and this may be the reaction involved in the decomposition of goethite:



Once water of constitution has been removed, the mineral from which it was released is virtually destroyed and no longer possesses the characteristics of the original form. Thus, kaolinite, $\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$ decomposes under conditions of slow rate of temperature rise at about 410°C . The resulting product is an intimate mixture of free silica and alumina, and although partial rehydration can be effected in an autoclave, the original form of the kaolinite has been destroyed. The reaction is as follows:



2. **Water of crystallisation** or **hydrate water** is that which is involved when substances of a crystalline nature are heated, usually at a comparatively low temperature. It differs from the combined water or water of constitution inasmuch as the original substance can be readily re-formed by treating the dehydrated material with water and then allowing it to recrystallise. The precise mechanism of the bonding of the hydrate water within the crystal is not known with certainty in all cases, but in many hydrates with ionic linkages water molecules are associated directly with the cation. These molecules are really dipoles which co-ordinate readily on positively-charged ions and undoubtedly many hydrates are of this form. The amount of water of hydration depends on the co-ordination around the cation, although the presence of anions introduces additional complication; a certain salt may form several types of crystals with different amounts of water of crystallisation, depending on the conditions of formation. Thus, hydrated sodium silicate occurs in three crystalline forms:

Formula	Crystalline Form
$\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$	rhombic
$\text{Na}_2\text{SiO}_3 \cdot 6\text{H}_2\text{O}$	monoclinic
$\text{Na}_2\text{SiO}_3 \cdot 4\text{H}_2\text{O}$	hexagonal

When a hydrate loses its water of crystallisation the atomic configuration is not entirely destroyed for it simply reverts to a non-hydrous form.

3. **Broken-bond water** is absorbed by crystals where there is a charge deficiency at a fractured edge. Kelley, Jenny and Brown¹ in 1936 were the first to introduce the term broken-bond water, and showed by dehydration experiments that it could be distinguished from true planar or adsorbed water.

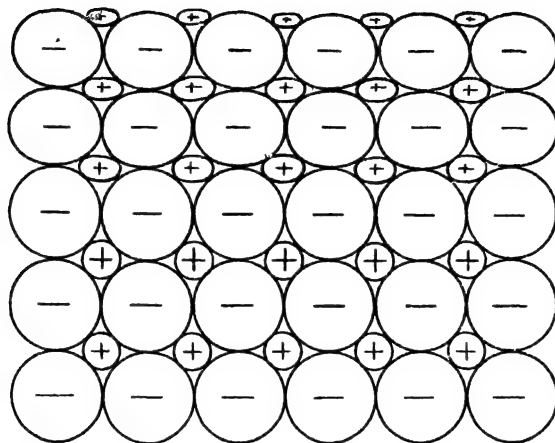


FIG. VIII.1. FIGURATIVE REPRESENTATION OF THE ATOMIC OR IONIC DISTRIBUTION IN THE SURFACE REGIONS OF CRYSTALS

At the broken edges of crystals, atoms or ions are exposed which cannot be in electrical equilibrium. If the crystal lattice is figuratively represented as a system of alternating positive and negative charges in three dimensions, as shown in Fig. VIII.1, an ion well-removed from the surface will be symmetrically surrounded in three dimensions by six ions of opposite charges, and thus will be in equilibrium. At the crystal edge, however, or along the line of a fracture the exposed ions are not surrounded on all sides, and the electrical balance is destroyed. It is on such centres, which, in most ceramic crystals will be mainly the larger negative ions of oxygen and hydroxyl units, that broken-bond water is held.

That water is absorbed by fractured surfaces can be readily illustrated by grinding many aluminosilicates. The product invariably gives a characteristic thermal pattern, which becomes more pronounced as the reduction in size is maintained. Apparently in the case of micas, feldspars and quartz, fracture takes place across the crystal, thereby exposing cations and anions which will not be electrically balanced. Hydroxyl or water molecules are absorbed from the surrounding atmosphere and strongly held. So firmly is the bonding between water of this type and the crystal edges, that it is only eliminated at high temperatures, and a type of compound formation must develop. Aluminosilicates which have been subjected to ball mill

¹ Kelley, W. P., Jenny, H. and Brown, S. M., *Soil Sci.*, 41, 272, 1936.

grinding show two thermal peaks at 550° C. and 225° C. The first is similar to that produced by the hydrates of alumina and the latter is associated with colloiddally precipitated silica. On prolonged grinding, the thermal peaks become more diffuse and water liberation takes place over a range of temperature.

4. **Colloidal water** may be regarded as the extreme case of broken-bond water. The particle size of the solid to which colloidal water is linked is extremely small. The unsaturated surface charges on the crystallites are numerous and able to influence not only those water molecules which are in contact, but also some removed a small distance from the surface. As the distance from the surface is increased, the binding forces decrease rapidly and consequently water molecules may be lost over a range of temperature. This is a characteristic of many colloidal gels, including silica and alumina, and, in addition, is a feature of some plastic clay pastes.

5. **Absorbed water** is water which is taken up within the crystal lattice on exposure to humid air. The most common example of a mineral with this capacity is montmorillonite, which has the property of absorbing moisture between the layers which make up the crystal. As a result, the lattice expands by virtue of the forcing apart by the water molecules.

The mechanism of the water-swelling of montmorillonites and some other layer lattice minerals has not been established with certainty, although several interesting theories have been advanced. Forslind¹ suggests that water molecules are arranged in the form of the ice structure which can fit between the layers of montmorillonite crystals provided that the Edelman-Favejee structure (see p. 146) is accepted. Hendricks and Jefferson² consider that the extra water molecules in hydrated halloysite $\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ have a definite structural arrangement with linkages to successive sheets of the kaolin-type. Méring³ is of the opinion, however, that in montmorillonites, the absorbed water is associated with the exchangeable base. Water molecules are considered to co-ordinate around the cations which are present between the layers. Mono- or di-molecular sheets can be recognised in calcium-bearing montmorillonite, but the sodium salt shows progressive hydration with increasing humidity. There is some support for Méring's conclusions from thermal analysis experiments on the hydrated forms of montmorillonite saturated with various ions. The peak corresponding to the loss of absorbed water occurs at different temperatures, which can be related to the exchangeable cation present. If this theory is accepted, then absorbed water is obviously closely related to water of hydration or crystallisation of salts.

The corresponding absorption of water in halloysite and possibly hydrogen montmorillonite, is not likely to be due to the same mechanism, for there are no exchangeable bases in the former mineral, and the hydrogen ion is too small to form co-ordinated groupings. It may well be that absorbed water does take on a specific structure which is determined largely by the 'fit' on to adjacent layers of the absorbing mineral, but where cations are present, they must exert some influence on the surrounding water molecules.

True absorption within the lattice is possible only in minerals which contain

¹ Forslind, E., *Meddelande*, No. 11, *Svenska*.

² Hendricks, S. B. and Jefferson, M. E., *Amer. Min.*, 23, 863, 1938.

³ Méring, J., *Faraday Soc. Trans.*, 42B, 205, 1945.

lattice holes of sufficient size to permit water molecules to enter (e.g. zeolites), or those which are capable of expanding to accommodate the molecule (e.g. montmorillonites). Such water is held more firmly than that resulting from simple surface adsorption and requires a slightly higher temperature before it is driven off; it is rapidly re-absorbed on exposure of the mineral to a humid atmosphere, provided that the mineral has not been decomposed by over-heating.

6. Adsorbed water is related only to the exposed surface-area of the mineral, and may thus be differentiated from absorbed water, which enters the crystal lattice. Because adsorption is restricted to the surface of minerals, it follows that its amount will be directly proportional to the surface-area of a material, and will be independent of its nature. This is not strictly so, although, for any particular mineral, the amount of water adsorbed is in direct relation to the degree of fineness of division, i.e. to the specific surface area. The amount of adsorbed water also depends on the humidity of the atmosphere to which the material is exposed and a change in humidity conditions is sufficient to alter its value.

By a mechanism which is not fully understood, the surface of all materials is capable of adsorbing a thin film of water molecules. It may be due to unsatisfied charges in the surface layers having a small binding action on water dipoles, which are thereby attracted and loosely held. More than one authority has suggested that a structure is induced in the adsorbed water film by the lattice configuration of the surface, and careful density determinations have established that such must be the case. Adsorbed, or hygroscopic water, as it is termed, is readily removed by gentle heat, or in the presence of certain desiccating agents.

Under normal conditions, the layer of adsorbed water is about 10 molecules thick. (This can easily be calculated from a knowledge of the specific surface area and percentage adsorption.) Therefore, the outermost sheets will be held less firmly than those closer to the clay surface—it has been stated that it is extremely difficult, if not impossible, to remove the adsorbed water which is directly in contact with the surface. The vapour pressure of such a layer would be expected to be very small, and therefore it would be retained, even at very high temperatures. So rigidly is this last vestige of adsorbed water retained that it behaves rather like broken bond, or colloidal water. The high dry strength of clays and other small-particled agglomerates is possibly due to the merging together of the rigidly-bound water layers.

7. Free water is that which is not combined in any way with the particles of the solid, and includes all excess water which may be present naturally or added during processing. It is frequently present as so-called *pore-water* which has been drawn into the mass of the material by capillary action. The maximum amount of pore-water is sometimes termed the *imbibitional moisture capacity*. When the raw material has been exposed to rain or excess water in another form, an even larger amount of water may be present, and in the case of clay, 'stickiness' develops. The physical concept of this state is that sufficient water is present in the interstices between the individual grains to cause partial separation. Deformation of the mass is, therefore, easy, as the water acts as a free-flowing cushion.

As more free water is introduced, the clay mass becomes plastic and will flow under its own weight. Finally, the clay/water mixture assumes all the characteristics

of a true liquid as the water content is further increased, until a slip or colloidal suspension is formed.

Free water in all its forms is readily lost on exposure to normal atmospheric conditions, for the partial pressure of the water present is invariably greater than the vapour pressure of water in the surrounding air.

The presence of free water, however, may change the complete character of the clay, and it is one of the principal processes involved in the 'weathering' of ceramic raw materials.

WEATHERING PROCESSES

THE changes in the physical state of clays and other ceramic materials, due to the application or removal of water in the ordinary course of nature, are commonly regarded as the result of 'weathering'. They include the action of rain, snow and frost in winter, and of sunshine and rain in summer—the former is sometimes known as 'wintering' and the latter as 'summering' or 'sunning', but it is convenient to regard all under the term 'weathering'.

It is sometimes desirable to increase the action which would take place during weathering and especially to increase its velocity. Such treatment may be regarded as *artificial weathering*. This includes such simple processes as 'watering' the clay with a hose-pipe, turning the material over to expose fresh surfaces, drying the material by artificial heat prior to exposing it to the weather or in order to reduce excessive plasticity, etc. When the action of cold water is not sufficiently intense, hot water or steam may be substituted.

Changes effected by Weathering. When clays and other raw materials used in the ceramic and allied industries are exposed for a sufficient time to the action of the weather, they may undergo one or more of the following changes:

- (i) Mechanical disintegration due to the freezing of water in the material.
- (ii) Physical changes which are dependent on the behaviour of water absorbed by the material.
- (iii) Chemical changes.

Most fired ceramic materials are highly resistant to the action of the weather and for that reason many of them are of great value for building and constructional work.

(i) *Mechanical Disintegration.* Dry clays and some other ceramic materials have the power of absorbing moisture from the atmosphere into their pores. If the weather becomes sufficiently cold the water is frozen, and as ice has a greater volume than the water from which it is produced, it exerts an enormous pressure on the ceramic material and may cause it to burst or disintegrate. Such an action is beneficial in the case of clays and some other materials, because it not only reduces the cost of crushing and grinding the materials, but it has the advantage over disintegrating machines, such as stone-breakers, crushing rollers, and grinding mills, in that the frost works from the inside outwards, instead of externally from the surface of the material towards the centre, and, consequently, produces effects which cannot be obtained by such machines. If sufficient time can be allowed most materials used in the ceramic industries may be disintegrated by frosty weather, but

the porous substances are most readily and rapidly disrupted, as water can more easily penetrate into the pores of such masses.

(ii) *Physical Changes on Weathering.* The principal *physical changes* wrought in clay by exposure to the action of the weather are:

(a) Moisture is absorbed up to the limit of the hygroscopicity and sometimes the imbibitional capacity of the clay.

(b) The moisture is more uniformly distributed.

(c) The cohesion of hard masses is decreased by the formation of water films which surround the individual particles and the consistency of the clay is changed.

(d) The plasticity is increased.

(e) Oxidation of some of the mineral and other constituents of the clay is a chemical change, but when it occurs the physical character is altered, e.g. a very sticky clay may become easier to work. As some iron minerals change their colour on exposure they may be more easily recognised and picked out of the weathered clay. Pyrites, on the contrary, may break down and be more difficult to separate.

Chemical action may change the type of clay or alter the amount of soluble salts and absorbed cations with a consequent change in the physical nature of the clay (see *Base Exchange*, p. 265).

Steaming has a similar effect on clay to exposing it to the action of weather. Its chief actions are to:

(a) Supply the water required by the colloids present in a form in which it can act more intensely than is possible with cold water.

(b) Secure the uniform distribution of moisture throughout the mass.

(c) Increase the temperature of the clay and so ensure a greater amount of fermentation of the organic matter present.

By these means, the plasticity and binding power of the materials are increased and the clay so treated is more easily shaped. When only a small amount of moisture is to be added to a clay it can be distributed more uniformly if applied in the form of steam. Some fireclays are much more readily disintegrated by steam or hot water than by cold water.

Water in its liquid state has a disruptive action on some ceramic materials, partly on account of its solvent action on the cementing or binding agent in them, and partly as a result of its direct mechanical action in penetrating between the grains. In both cases, its action is so slow that many years are required for an appreciable action to take place in non-plastic materials, and for that reason there is little to be gained by exposing them to the weather for only a month or two. Where a non-plastic deposit which has been weathered for many years is available, its value is often much greater. In some non-plastic materials, a chemical change, such as the oxidation of impurities, may occur. Clays differ from the materials just mentioned in being very sensitive to the action of absorbed water, as they are both hygroscopic and porous, whilst sand and silt are much less hygroscopic and only absorb a very small proportion of moisture from the atmosphere. When clay is left exposed to the atmosphere, it absorbs up to 20 per cent of its weight of water without appearing to be wet, and it is almost impossible to keep a fully-dried clay

perfectly dry, unless special precautions are taken to keep it out of all contact with moisture.

Distribution of Moisture. The water in raw clays is seldom uniformly distributed, and it requires a considerable amount of time before uniformity can be secured, especially with highly plastic clays, such as ball clays. For this reason, it is customary to allow some clays to be exposed to the weather for several months, and in some instances for several years, before using them.

The time taken to weather different materials properly varies greatly according to their nature. Thus, a comparatively soft clay may merely require to remain exposed to the weather for a few days or weeks. Other materials, such as hard shales, require two years or even more. Many shales used for making bricks are exposed for at least a year and a half before using, whilst some Broseley and some Stourbridge clays are weathered for two or three years.

Some clays are very peculiarly affected by weathering; thus, some of the Durham clays—especially those from the Five Quarter and Bottom Busty seams—become less plastic the longer they are exposed. Some of the clays used for making tiles in the Midland counties are adversely affected by weathering in wet weather. Where possible, the clay should be dry before it is exposed to the weather, as it is then in a more permeable state. Clay which has been wetted on the surface may be quite impermeable to water and, therefore, unaffected by rain. The best conditions are obtained when a dry clay is immersed in water and thereby thoroughly saturated prior to exposure to the weather. Such a procedure is seldom practicable, so that the best method generally available is to spread it out in comparatively thin layers and expose it directly to the action of rain, frost and snow. If the exposure is continued during fine weather any excess of moisture will be gradually removed by the atmosphere, the clay retaining only sufficient water to saturate it hygroscopically.

Disintegration. The disruptive effect of frost and the softening action of absorbed water will together reduce the cohesion of a clay to such an extent that most clays, after weathering, will mix much more readily with water when treated in the ordinary mills and mixing machines, and will, consequently, produce a more even and uniform paste than can be made from clays which have not been weathered.

(iii) *Chemical Changes on Weathering.* The chief *chemical effects* which occur on weathering are caused principally by the agencies of air and water, although some reactions are catalysed by sunlight. These are as follows:

(a) The solution and replacement of some substances after oxidation and hydrolysis.

(b) The oxidation of carbonaceous matter, sulphides and some ferrous compounds.

(c) The hydration or hydrolysis of substances which are ordinarily insoluble.

Solution and replacement by water has an important effect in changing the chemical nature of rocks through which it percolates, especially when it contains dissolved substances in solution. Thus, the percolation of water containing carbon dioxide through clay beds may cause the solution and removal of any soluble substances present. For instance, calcium carbonate may be removed in this way from a highly calcareous clay or clayey limestone, and it is generally thought that the

pocket clays of Derbyshire are composed of the insoluble residuum from a clayey limestone, the greater part of which has been removed by the solution of the calcium carbonate. Some clay beds containing calcium carbonate are richer in this impurity near the bottom of the bed than at the top, this latter portion having been partially purified by carbonated water descending from the surface and dissolving the calcium carbonate in its passage.

Even silica—though normally regarded as insoluble in water—is not wholly so.

The disintegration of rocks and clay beds by weathering is largely, though not entirely, due to the removal, in solution, of soluble substances originally present as bonding material.

Conversely, water containing silica in solution, when in contact with siliceous rocks, tends to permit the precipitation of the silica in the pores of the rock, with the result that the particles of aggregate are still more firmly united with a siliceous cement. As water can contain both silica and calcium bicarbonate simultaneously in solution, a limestone may have part of its calcium carbonate removed in solution by percolating waters and replaced by silica—chiefly in the form of chert. Thus, near Carlow, in Ireland, a bed of chert 30 to 40 feet thick has replaced the original carboniferous limestone. The flints and chert in some English chalk and limestone beds are due to metasomatic replacement of this character. Sometimes quartz is replaced by calcite brought in solution by percolating waters, but this type of replacement is not common.

Another typical rock formed by partial replacement is dolomite, which has been formed by the substitution of some of the calcium carbonate in limestones by magnesium carbonate. Some dolomites, however, appear to have been produced by simultaneous crystallisation of both magnesium and calcium carbonates (see p. 325).

Weather has a bleaching action on clays and some other minerals containing suitable carbonaceous matter, because the latter, when decomposing as a result of exposure to air and water, forms humic acid and other acids which dissolve some of the iron and other compounds and remove them in solution.

Prolonged exposure to the weather also results in the solution and removal of selenite and gypsum. Any other soluble salts in a clay or other ceramic material may also be dissolved and carried away by water percolating through the mass.

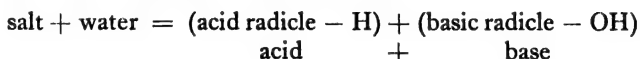
Cementation, or the binding of the particles of aggregate into a strong mass of rock by means of a binding agent or 'cement', is caused, by (a) the mingling of solutions from different sources, as when a solution containing oxygen comes into contact with one containing iron compounds in solution, the result being the precipitation of iron oxide and the cementation of the rock in which the precipitation occurs; (b) the chemical reactions which occur between rocks and solutions percolating through them. Thus, the action of water upon anhydrous rocks causes the formation of hydrates or hydroxides, which fill up the pores and cement the rock particles. For example, feldspar may be replaced by zeolites or haematite by limonite. Temperature and pressure play an important part in modifying the effect of chemical reactions in cementation.

Oxidation. Exposure to weather (i.e. to water and air) converts ferrous compounds into the ferric state, limonite being the chief product. Iron sulphides are, to some extent, converted into sulphates, marcasite being more readily oxidised than

pyrite. Copper sulphides are oxidised in a similar manner, erubescite being readily broken down and chalcopyrite with more difficulty.

Sunlight appears to favour oxidation and has therefore an important influence on the weathering of clays. Remarkable differences in the character of some clays occur even after a few hours' exposure to sunlight and air, whilst other clays are scarcely affected. The difference is apparently due to some oxidation processes, possibly associated with colloidal changes accompanying the hydration of the material, but the precise nature of these changes can only be surmised, as they have not been fully investigated.

Hydrolysis is a term used rather loosely to indicate the effect of water in decomposing various substances as well as in forming additive compounds; the latter is usually termed *hydration*. Both are really the reverse of the neutralisation of an acid by a base, and may be expressed by the equation:



Thus, in hydrolysis, a salt splits up, forming an acid and a base or, occasionally, a basic salt. The duration of the exposure to water and the enormous masses involved enable changes to take place in nature which cannot be accomplished in the chemical laboratory, with the result that most silicates and oxides can be hydrolysed and compounds, such as clays, formed, which cannot be produced by any artificial means. In the same way, the hydrolysis of iron compounds in clays and other rocks sometimes results in the formation of a particularly strong ferruginous cement. The yellow films or stains widely distributed among rocks are due to the production of limonite (see p. 278) by the oxidation and hydrolysis of other iron compounds.

Base Exchange. One of the most important consequences of weathering processes is the changes in the exchangeable bases. The influence of the type and amount of absorbed cation is discussed more fully in a later section of this Chapter.

Other Physical Processes due to Water.

1. *Slaking and Swelling.* When a 'lump' of clay is immersed in a large volume of water it gradually softens and eventually falls to a soft 'mushy' mass. This change is known as 'slaking'; it has an important practical significance, because those clays which slake rapidly can be easily tempered or mixed with water to produce a homogeneous paste.

The time required to slake a clay varies according to the porosity of the material and the cohesion of the particles. A soft, porous, lean clay may be completely slaked in a few minutes, but a hard clay-shale or a highly plastic material may not be fully disintegrated after several weeks. The speed of slaking is increased if the water used to effect it is slightly alkaline.

Sokoloff determines the rate of slaking of a clay by mixing it with various proportions of sand, making these mixtures into small pyramids, which are thoroughly dried at 100° C. and then allowed to stand on a small wire grid immersed either in still or running water, until the mixtures have completely broken down. Running water is best for plastic clays, as it is difficult to see the end point in still water on account of the turbidity of the liquid, whereas the running water removes the finest particles as the test-pieces disintegrate.

The slaking is usually accompanied by an increase in the volume of the mass and a small rise in temperature.

2. *Swelling*, is the term applied to the increase in volume when a clay is immersed in water. It is caused by the absorption of water within the crystal lattice of certain minerals, particularly those of the montmorillonite and related layer-lattice crystals (see pp. 150 and 419).

Although the absorption of water is theoretically reversible, and the separation between layers of the crystals returns to the normal value when the water is removed, a permanent increase in the overall volume always remains on drying the swollen mass: this is probably the result of disruption within the mass caused by unsymmetrical drying.

The amount of swelling which occurs when a clay is treated with water depends on many factors which include (a) the type and amount of clay minerals which are present; (b) the exchangeable ions associated with the clay; (c) the particle shape and size of the clay; (d) the texture of the mass; (e) the soluble salts in the water, and (f) any superimposed load on the swelling mass.

Of the clay minerals, the montmorillonites swell to a far greater extent than other types. Sodium montmorillonite expands much more than the same clay mineral saturated with other ions and the rate of swelling is maintained for long periods of time (up to several weeks). Such effects can have serious consequences when buildings or roads are constructed on soils rich in these minerals and there are many examples of disruption being caused when water percolates to the foundation materials in such cases. Mielenz and Okeson¹ studied the foundation displacements which occurred along the Malheur River siphon and found a progressive uplift which sometimes exceeded 1 foot in three years. The constructions were over a sodium bentonite and uplift pressures of the order of 7,200 pounds per square foot were recorded, which lifted not only the siphon but 38 feet of alluvial sand and silt as well.

The water swelling capacity of montmorillonite finds application in oil-drilling processes in which the swollen clay is used to seal porous rock-formations.

Swelling also occurs when dry clays are immersed in various organic liquids. The expansion of the basal spacing of montmorillonite by ethylene glycol,² from 14 Å to 17 Å is distinctive and is a valuable means of identifying this mineral, but aliphatic amines are even more effective,³ provided that they contain a chain of 10 carbon atoms or more. The lattice is expanded by about 8 Å, suggesting that two molecular layers can be absorbed. An expanded montmorillonite is highly absorbent and has other characteristic and valuable properties.

3. *Heat of Wetting*. When dry clay is mixed with water, alcohol or various organic liquids, a rise in temperature occurs due to evolution of heat. This 'heat of wetting' is commonly called Pouillet's⁴ effect, but Leslie⁵ observed it twenty

¹ Mielenz, R. C. and Okeson, C. J., *Econ. Geol.*, **41**, 266, 1946.

² MacEwan, D. M. C., *X-ray Identification and Crystal Structure of Clay Minerals* (Mineralogical Society, London, 1951), Chapter 5.

³ Jordan, J. W., Hook, B. J. and Finlayson, C. M., *J. Phys. and Coll. Chem.*, **54**, 1196, 1950.

⁴ Pouillet, *Ann. Chim. Phys.*, **20**, 141, 1822.

⁵ Leslie, *Tilloch's Phil. Mag.*, **14**, 201, 1802.

years earlier. According to Adam¹ it may be represented by the equation:

$$u = W - T \frac{dW}{dt}$$

where u is the heat of wetting per unit surface, W the work required to separate the two surfaces (i.e. work of adhesion), and T the temperature in absolute degrees. The term

$$-T \frac{dW}{dt}$$

is sometimes known as the *latent heat of the surface*; it is the amount of heat which has to be applied to the surface to maintain it at a constant temperature.

Although many other factors are involved, the heat of wetting can be related directly to the surface area of the powder by the expression

$$H = h \cdot S_A$$

where h is a constant depending on the nature of the liquid and surface (i.e. the heat evolved when 1 sq. cm. of surface is wetted with a specified agent) and S_A is the total surface area which is wetted. In recent years² attempts have been made to measure the surface area of powders by the use of such methods, but owing to the uncertainty in the value of h and the amount of heat generated, the method has only a limited application.

Harkins and Boyd³ have attempted to deduce values of h for several solids and liquids, and find values lying between 100–500 ergs cm.⁻¹. On this basis, the heat of wetting of powders with an average particle size of 1 micron would lie between 0.07 and 0.35 cal. per gm.

The method of determination presents considerable experimental difficulty. Normal calorimetric methods using a Beckmann thermometer have been employed, although better results can be secured by measuring the temperature rise with a set of thermocouples,⁴ arranged as in a thermo-pile, but with a very small heat capacity.

The heat of wetting of a relatively pure china clay is about 2 calories per gram, and 600 calories per gram of plastic clay, whereas Parks⁵ found that the heat of wetting of silica powders by water is only 0.00105 calories per gram.

Detergent action. A property of clay which is seldom realised is its power of reducing the surface tension of water. By this means it enables water to wet surfaces more readily than when the water is used alone. One technical advantage derived from this property is that sometimes mixtures of clay and soap have the same detergent action as soap alone, so that clay added to soap to cheapen it, is not merely a diluent, but has a definite cleansing power.

In former times when only crude and very alkaline soaps were available, the use of clay and water for cleaning (fulling) wool was very common and yielded a softer

¹ Adam, *Physics and Chemistry of Surfaces* (Oxford, 1930).

² Gregg, S. J., 'Symposium on Particle Size', *Inst. of Chem. Eng. and Soc. of Chem. Ind.*, 1947, p. 40.

³ Harkins, W. D. and Boyd, G. E., *J. Amer. Chem. Soc.*, **64**, 1195, 1942.

⁴ Clark, A. and Thomas, B. D., *J. Phys. Chem.*, **43**, 579, 1939.

⁵ Parks, *Phil. Mag.*, **4**, 240, 1902.

and plumper product than when soap was used. Hence the term *fullers' earth* for certain montmorillonite clays which have long been used for this purpose.

Emulsifying action. Clay has a powerful emulsifying action, i.e. a mixture of oil and water which, alone, would rapidly separate into its two constituents, remains as an emulsion in the presence of about 1 per cent of clay. Plastic clays are the most effective for this purpose.

The principal effect of adding water to clay is, however, the plasticity or stickiness which is induced. It is in this sense that clay behaves as a true colloid and this physical phenomenon can be explained only by a consideration of such systems.

THE COLLOIDAL STATE

IN the last few decades the study of colloidal suspensions has been advanced to such an extent that it is now a science in its own right. Within the limits of this volume it is possible to give only the briefest description but it must be remembered that clays are only one of many colloidal systems, each of which has certain characteristics.

The existence of colloids was first demonstrated by Graham¹ in 1861. He showed that, whereas a true solution of a soluble salt would pass freely through a parchment membrane, other substances such as glue, starch, and silicic acid, although they appeared to go into solution, would not penetrate the membrane. Graham called these bodies which would not dialyse, *colloids*, after the Greek, *kolla* (glue) and *eidos* (the form).

This classification is now known to be not strictly correct, for it is possible to obtain virtually any substance as a colloid under suitable conditions.

A colloidal solution may be defined in general terms as a suspension of particles in a liquid, where the grain size of the solid is so small that they will not settle, yet at the same time they cannot be regarded as being in true solution.

Various types of colloidal solutions are known within the three physical states of matter, gas, liquid and solid. Thus, mist, fog and steam are examples of a suspension of liquid in a gas (air); smoke is a suspension of solids in gas; foams and emulsions are gaseous components in liquids; the colloidal solution of a solid in liquid is exemplified by a clay-water system. Although the ultimate particles in a true colloid are too small to be seen with the naked eye or even under the magnifications of an optical microscope, they are clearly revealed by an ultra-microscope in which a narrow beam of light, shining through a colloidal solution, is reflected from the particles and thus characteristic turbidity is produced. A comparable effect may often be observed when a shaft of sunlight picks out fine dust particles in a still atmosphere. This is known as the *Tyndall effect*.

The grain size of particles in a true colloid is within the range of Brownian movement, or in other words, they are small enough to be influenced by collisions with the molecules of the liquid (or suspending) medium, and are in a constant state of agitation. There are no fundamental limits to the size of such particles, but W. Ostwald has suggested that the maximum size is 0.001 mm. and the minimum size 0.000001 mm. Particles much less than this minimum may have colloidal properties, but they chiefly occur in true solution as ions, atoms or molecules, though

¹ Graham, T., *Phil. Trans. Roy. Soc.*, London, 151, 183, 1861.

the difference between some colloidal solutions of very low concentration and some 'true solutions' is not very distinctive.

The present practice is to regard 0.2μ (0.0002 mm.) as the maximum size of particles of colloidal dimension to a minimum of 0.005μ (0.000005 mm.) though some investigators prefer to use other figures.

It is important to realise that some clays, whilst consisting of particles larger than those included as colloids, have so open and spongy a structure that they behave like colloidal particles. This is particularly the case with some clays of the montmorillonite type, including some fullers' earths.

The properties and differentiating characteristics of a colloidal suspension are:

1. The particles are not visible except in an ultramicroscope.
2. The particles will not dialyse (i.e. pass through a membrane).
3. The grain size can apparently be altered by electrolytes. The addition of certain soluble salts will cause *coagulation*, or settling out of the suspended particles.
4. The viscosity of a colloidal suspension is invariably greater than that of the suspending medium, which is not always the case in a true solution.

Many substances show unusual properties in the colloidal state. For example, the exceptional turbidity of zinc oxide when in the form of particles of colloidal dimensions is of value in the production of some opaque glazes and in the paint industry. Similarly an aggregate of carbon particles has been shown to have a maximum hardness value when the grains are of colloidal size.

To be a true colloid the ultimate particles must be smaller than 0.2 microns (1 micron = 10^{-4} cms.) in size, and it is only when grains of these dimensions are present that suspensions show anomalous properties. Some answer to the reasons why exceptionally small particles behave differently from larger-sized ones is shown by a study of their crystal form. Crystallographers have concluded that all crystals are built of fundamental units which are termed *unit-cells* (see Chapter II). The more complex the atomic arrangement, the larger will be the unit cell, and therefore, the less will be the number of units required to form crystals of appreciable size.

Taking calcium fluoride, CaF_2 , as an example, the unit cell of which is shown in Fig. VIII.2, there are fourteen atoms of calcium and eight of fluorine. If two unit cells are joined together to share a common face containing four calcium atoms, the ratio of calcium atoms to fluorine atoms is $63:64$. As more units are added, the ratio of the two kinds of atoms approaches the stoichiometric $1:2$ as predicted from the formula CaF_2 . However, many units have to be linked before this condition is reached, as shown by Table VIII.I.

TABLE VIII—I. RATIO OF NUMBER OF CALCIUM ATOMS TO FLUORINE ATOMS IN CRYSTALS OF CALCIUM FLUORITE, CaF_2 , WITH INCREASING CRYSTALLITE DIMENSIONS

Number of unit cells n .	Number of calcium atoms N_{Ca}	Number of fluorine atoms N_{F}	$\frac{N_{\text{F}}}{N_{\text{Ca}}}$	Length of side of crystallite in millimicrons
1	14	8	0.572	0.62
5	663	1,000	1.510	3.10
10	4,631	8,000	1.729	6.2
1,000	4,060,301	8,000,000	1.971	62

Thus, in a comparatively simple crystal, the stoichiometric ratio is not exactly obeyed until the crystallite size is quite large (0.1 microns). When more complex crystals are considered, where the unit cells are large, there is great deviation from the true atomic ratios, because particles of colloidal dimensions are, in some cases, composed of only a few unit cells. Consequently, normal chemical laws cannot be applied to colloidal systems, and the concept of electrically-balanced crystals does not hold. Balarew has carefully analysed highly-dispersed precipitates, and has proved to some extent the failure of stoichiometric laws when applied to colloidal suspensions.

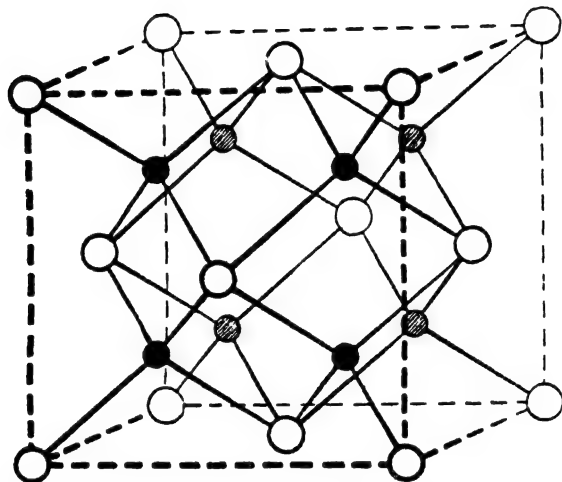


FIG. VIII.2. THE UNIT CELL OF CALCIUM FLUORIDE, CaF_2 . Large circles represent calcium ions and small ones fluorine

The most important feature of colloidal particles is the extremely high surface area relative to their volume. It has been shown in Fig. VIII.1 that the outermost layers of atoms or ions of a crystal are not completely balanced electrically. It might be expected that the properties of such surfaces would differ from the inner balanced layers of crystals. This is in fact so and Weyl has demonstrated the abnormal properties of surfaces due to the inadequate screening of atoms and ions.

In particles where the distorted surface layers are an appreciable proportion of the whole mass (i.e. colloidal particles) it is to be expected that they will be abnormal in behaviour.

The increase in specific surface area with decreasing particle size is illustrated on p. 472.

The specific surface area (or area per unit weight) of particles of 0.1 microns diameter will be 10,000 times greater than that of spheres of 1 millimetre.

Colloidal solutions are generally recognised as being of two types:

(a) **lyophilic** (meaning 'liquid loving'), and (b) **lyophobic** (implying 'liquid hating'). When water is the suspending medium then these two forms are frequently

called *hydrophilic* and *hydrophobic* sols respectively. The properties of the two types are very different, although many colloidal solutions will, under varied conditions, show properties associated with both groups.

The main features of lyophilic and lyophobic sols are compared in Table VIII.II.

TABLE VIII—II. PRINCIPAL PROPERTIES OF LYOPHILIC AND LYOPHOBIC SOLS

<i>Lyophilic</i>	<i>Lyophobic</i>
<ol style="list-style-type: none"> 1. The surface tension is often much lower than that of the dispersion medium. 2. The viscosity is much higher than that of the dispersion medium. 3. Small quantities of electrolyte have little effect, although larger amounts may cause 'salting-out'. 4. Particles are not easily detected. 5. Particles may migrate in either direction in an electrical field (or not at all). 6. The suspension is easily reversible after drying. 	<ol style="list-style-type: none"> 1. The surface tension of the suspension is similar to that of the dispersion medium. 2. The viscosity is not very different from that of the dispersion medium. 3. Precipitation is achieved even with small amounts of electrolyte addition. 4. Particles are readily 'observed' in an ultra-microscope. 5. Particles are all of one charge and migrate readily in one direction in an electrical field. 6. After drying, the suspension is not readily reconverted.

No hard and fast rule can be laid down as to whether a particular colloid will be hydrophobic or hydrophilic. In general, metal sols are of the first group, whilst complex organic materials, e.g. starch, glue, are the best examples of the latter.

For the most part, clay minerals form hydrophilic sols, but their properties are not always consistent with those expected from suspensions of this type. Colloidal particles of clay minerals are mostly negatively charged and in addition they are sensitive to small additions of electrolytes. Clay minerals have the capacity to adsorb and absorb other substances from suspensions and these materials often have a pronounced influence on the colloidal properties of the clay. Aliphatic amines, particularly those with a long carbon chain, e.g. dodecylamine $C_{12}H_{25}NH_2$, are absorbed by montmorillonite clays and form true hydrophobic sols; in this form, clay minerals are water resistant, but have a greater capacity for absorbing organic substances.

FORCES ACTING ON COLLOIDAL PARTICLES

VARIOUS forces act on colloidal particles suspended in a medium, and these determine the behaviour of slips and slurries which are essentially fine-particled suspensions.

(a) **Van der Waal forces** set up an attraction between particles. The larger the size or weight of the particles, the greater will be these forces, but in a system where the grain size is small, they will not predominate unless the particles approach closely to each other.

(b) **Gravitational forces** tend to cause sedimentation; the larger the particles, the greater will be the effect of these gravitational forces.

(c) **Thermal movement** of particles opposes the forces of attraction, although it is appreciable only when the particle size is extremely small and it rapidly decreases with increase in size, but it predominates in highly dispersed sols.

Little is known about the relative effect of these three forces, but von Buzagh suggests that if these were the only forces acting, then with particles of colloidal dimensions there would be a strong tendency for coagulation to take place; at the size of colloidal particles, the net attractive force will be at a maximum, implying that particles will more readily come together and aggregate. The fact that stable colloidal suspensions do exist, indicates that other forces must be operative.

(d) Colloidal particles, in the majority of cases, possess an **electrical charge**. In an electrical field, therefore, such particles behave in a similar fashion to simple ions—they migrate in a particular direction. This phenomenon is known as *electrophoresis*, and when all particles are negatively charged, the phenomenon is termed *kataphoresis*. Such particles mutually repel and prevent coagulation.

When suspended in a liquid medium, many particles, by virtue of their inherent charge, will adsorb a film of the liquid. Although its thickness is not very great, it acts as a cushion and prevents the close approach of the individual grains of solid suspended matter. The nature of the forces which are present in the *lysophere*, as the liquid film is termed, will be outlined in the next section, but its existence can be proved by a simple experiment. Finely-grained quartz (less than 200 B.S. sieve size) is a suitable raw material for demonstration purposes and it should be thoroughly dried out prior to testing.

A fixed weight (about 20 gms.) should be placed in each of several identical cylinders. To each of these should be added a different liquid—a useful series is water, ether, toluene and carbon tetrachloride. Excess of liquid should be used to ensure that after the solid has been thoroughly wetted and saturated, some free liquid remains above the sedimented powder. After prolonged shaking, the powder in each cylinder is allowed to settle and its sedimentation volume then measured; a different value will be observed with each liquid. The sedimentation volume per gram of the particular powdered quartz crystal in each liquid was as follows:

TABLE VIII—III. VOLUME OF SEDIMENT IN VARIOUS LIQUIDS

<i>Liquid</i>	<i>Water</i>	<i>Ether</i>	<i>Toluene</i>	<i>Carbon tetrachloride</i>
Sedimentation vol. per gm.	0.83	1.15	1.22	1.28

The packing density of the powder in air, when presumably all particles were in contact was 1.39, which gives a sedimentation volume per gram of 0.72.

The increase in the sedimentation volume of the solid particles on settling in the various immersion liquids is due to a film which has been formed around the particles. The thickness of the lysophere depends on the nature of the liquid used. Of the liquids shown in Table VIII.III the lysophere is thickest with carbon tetrachloride.

The formation of a lysosphere is a characteristic of the immersing liquid and also of the surface of the solid particles and consequently, the smaller the particle size the greater will be the volume of the lysosphere per unit weight of sample. With grains of colloidal dimensions, the thickness of the adsorbed liquid film is so great that in many respects the lysosphere behaves as though it were a rigid layer preventing the close approach of individual particles. When water is the suspending medium, the liquid film surrounding particles is termed a *hydrosphere* and this hydrated layer is responsible for many of the intriguing properties of colloids.

THE COLLOIDAL MICELLE

COLLOIDAL particles when suspended in water are charged and are surrounded by a water shell. The molecules of water within this shell are rigidly held by the particle and have a different character and properties from those in the remainder of the dispersion medium. The water shell may also contain cations and anions which play an important part in determining the behaviour of the colloidal suspension. Because of the intimacy of the association of the solid particle with its hydrosphere, it is convenient to regard these *colloidal micelles*, as the basic units in colloidal solutions.

The origin of the charge on particles can, to some extent, be explained from a study of the nature of the raw materials. The crystal structure of clays and other silicate minerals has been illustrated in Chapter III, but it is sufficient here to recall that the essential components are large anions (negatively-charged ions) of oxygen and hydroxyl units held together by much smaller cations (positively-charged ions).

A cleavage section of a kaolinite crystal (see p. 129) will be along the basal plane, exposing layers of oxygen and hydroxyl units, although only weak bonds are broken in the process. Fracture across a plate of these layer minerals, however, breaks valency bonds between the cationic and anionic components. As the negatively-charged ions are very much larger than the positively-charged ones, the former predominate in the external layer. The net result of this, and the fact that hydroxyl units themselves are also adsorbed, is that the surface of clay particles and related minerals is negatively charged when suspended in a water medium. Consequently, it will attract cations and as a direct result the surrounding regions of the water medium in the immediate vicinity of the particles will be rich in positively charged ions which counter-balance the surface charge and maintain electrical neutrality. Helmholtz¹ was the first to recognise this important principle, and he postulated that a *rigid double-layer* was formed in close proximity to the clay surface as illustrated in Fig. VIII.3. Although Helmholtz's theory was a logical deduction, there were many shortcomings in the concept of a rigid monomolecular layer associated with the surface.

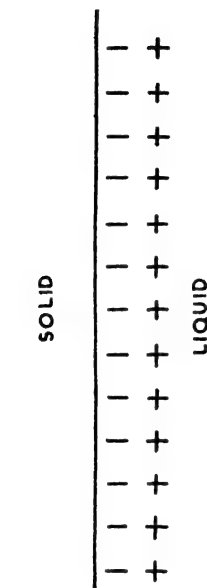
Gouy² and Freundlich³ suggested that the layer of cations was not so sharply defined in thickness as Helmholtz supposed and introduced the *diffuse double-layer theory*. They maintain that the double layer is not limited to the layers of the hydrated shell in intimate contact with the surface, but extends some distance into

¹ Helmholtz, H. V., *Wied. Ann.*, 7, 337, 1879.

² Gouy, G., *J. Phys. Radium.*, 9, 457, 1910.

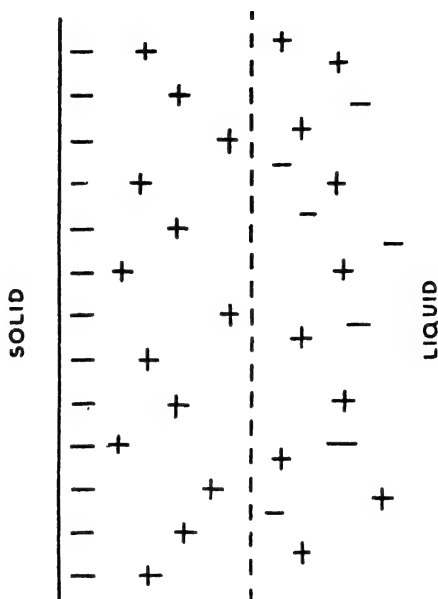
³ Freundlich, H., *Kapillarchemie*, Vol. 1, 4th edition (Leipzig, 1930.)

the liquid medium. In other words, the counter-ions in the liquid are not statically held in close contact with the surface but are diffused throughout a finite volume of the liquid medium (Fig. VIII.4). Gouy considers that the cationic distribution falls off exponentially as the distance from the surface is increased. Thus a type of atmosphere is set up round the surface.



HELMHOLTZ
DOUBLE LAYER

FIG. VIII.3.
THE HELMHOLTZ RIGID
DOUBLE LAYER THEORY



GOUY - FREUNDLICH
DOUBLE LAYER

FIG. VIII.4.
THE GOUY-FREUNDLICH DIFFUSE
DOUBLE LAYER THEORY

In the particular case of a clay suspended in water this ionic concentration gives rise to a secondary effect which limits the close approach of the cation to the surface of particles and gives rise to the diffuse double-layer. As a result of the intense electrical forces in the vicinity of the surface the molecules of the suspension medium are themselves oriented, giving rise to a layer of rigidly-held liquid. As the distance from the surface is increased, the degree of orientation of the molecules of the suspension medium decreases at the same rate as the concentration of counter-cations. The variation in these properties is a function of the surface and the type and concentration of the ions in solution.

Freundlich has investigated the electrokinetical laws which govern the variation in charge density at points extending outwards from the surface of charged particles and his conclusions are shown figuratively and graphically in Fig. VIII.5 in which the charge on the surface is regarded as $20e$ represented numerically by the point A

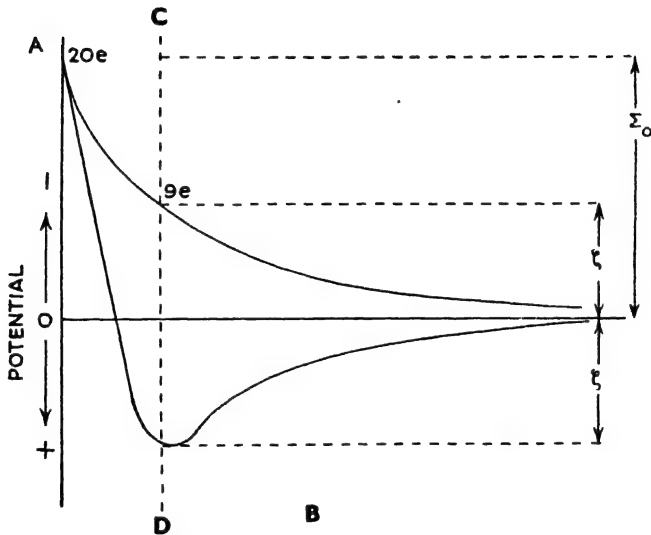
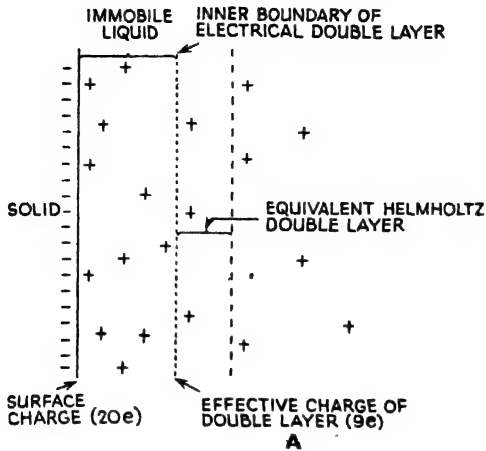


FIG. VIII.5. THE POTENTIAL ENERGY ASSOCIATED WITH A CHARGED SURFACE

on the *ordinate* with O as the point of zero charge. Distances from the surface layer are represented along the *abscissa*. The influence of the charged surface falls rapidly with separation distance to a zero point, which represents the condition of charge in the suspension medium entirely removed from the influence of the surface. Two of the ways in which the potential drop may take place are shown in Fig. VIII.5B. In the first, the concentration of ions of opposite charge to the surface which are held in the layer of rigidly-held water, is not sufficient to neutralise the charge which progressively falls to zero in the free water zone. In the second case, the ionic concentration

in the orientated water layer is such that a reversal of charge takes place but, once again, there is a progressive decrease in the charge at distances outward from the surface. The edge (CD) of the rigidly-held water may be regarded as one plate of an imaginary condenser, the other being the point in the liquid where the charge has fallen to zero. Whereas Helmholtz imagined that this imaginary condenser was virtually a monomolecular layer thick, the Gouy-Freundlich conception is of a diffuse

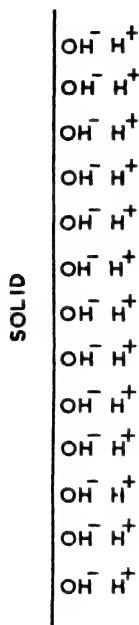


FIG. VIII.6. THE DIFFUSE DOUBLE LAYER
WHEN HYDROGEN IS THE
COUNTER-BALANCING CATION

layer extending away from the surface. The electrokinetic potential of the 'condenser' or the *zeta*-(ζ)-potential as it is known may be expressed simply by the relation derived by Müller and Abramson¹

$$\zeta = \frac{4\pi ed}{D}$$

where e is the surface density of charge, d is the thickness of the layer, and D is the dielectric constant of the medium.

The zeta-potential is a measure of the magnitude and extent of the forces arising as a result of the electrical charges on a particle. The surface density of charge (e) is a function of the type of surface and the ions which are present in solution.

Each colloidal micelle in a suspension will be surrounded by a hydrated shell and provided that the solid particles are of one type, each particle will have a charge

¹ See Abramson, H. A., *Electrokinetical Phenomena and their Application to Biology and Medicine* (New York, 1934).

of the same sign. Consequently, repulsive forces will be set up between all suspended particles, the magnitude and extent of which will depend on the zeta-potential. It is not surprising therefore, that many of the features of colloidal suspensions can be related to this value.

In the simplest case of a clay suspended in pure water, negative hydroxyl ions will be adsorbed on the surface and the counter ions are the hydrogen ions (H^+) which make up the diffuse double-layer represented in Fig. VIII.6. As hydrogen ions are small, there can be little hydration, and few oriented water molecules to form a rigid layer. Conditions are favourable for the close approach to the surface of sufficient hydrogen ions to neutralise the charge; hence in an hydrogen clay suspended in pure water the hydrosphere surrounding the colloidal particles is small. In addition, the dielectric constant of pure water is relatively high, so that the zeta-potential is low. In such a system the repulsive forces between particles are very limited in extent, and individual particles can approach closely to each other without being repulsed. If the conditions in a colloidal system are such that the repulsive forces between micelles operate at only small separation distances, the particles may approach one another so closely that van de Waal attraction forces become effective and cause aggregation and complete precipitation, i.e. *flocculation*.

FLOCCULATION AND COAGULATION

The term *flocculation* implies the gathering of particles into 'flocks' which settle rapidly, leaving a clear liquid. This distinguishes it from *coagulation* in which particles unite to form larger ones which do not necessarily settle rapidly. Both terms are used rather loosely.

Deflocculation is the reverse phenomenon, i.e. the dispersion of the aggregation into small particles which remain in permanent suspension.

The zeta-potential is the factor which governs the stability of suspensions of clay particles. Tuorila¹ has compared the ease of flocculation or coagulation with the zeta-potential of kaolinite clay suspensions, and his results are shown graphically in Fig. VIII.7. Below a certain value of zeta-potential, collisions between particles are presumably possible although they are not frequent, hence aggregation is slow. Further reduction in the value enhances the probability of collisions and the rate of flocculation is very much increased.

Sols and Gels. A stable colloidal suspension is termed a *sol*, and the particles in them, although solvated, have independent existence and show Brownian movement. If such a sol is precipitated or coagulated the particles do not settle to form a dense layer, but the whole colloidal suspension sets to a semi-solid state called a *gel*. The amount of water contained in such a body is very large, but the nature of gels and the intimacy with which the particles and the water are associated is largely unknown although there are many theories, most of which have been outlined by Williamson.² Gels are formed only by small-particled materials and some authorities³ consider that they are the ultimate cause of plasticity (see p. 465) in clays. When a gel forms

¹ Tuorila, P., *Kolloidchem. Beihefte*, 27, 44, 1928.

² Williamson, W. O., *Trans. Brit. Ceram. Soc.*, 50, 10, 1951.

³ Webb, H. W., *Trans. Brit. Ceram. Soc.*, 33, 129, 1934.

Brownian Movement ceases, which suggests that a type of balanced structure has formed; Hauser and Reed¹ postulate that the solid particles are held in an equilibrium position by attractive and repulsive forces and that water molecules occupy the holes in such a structure.

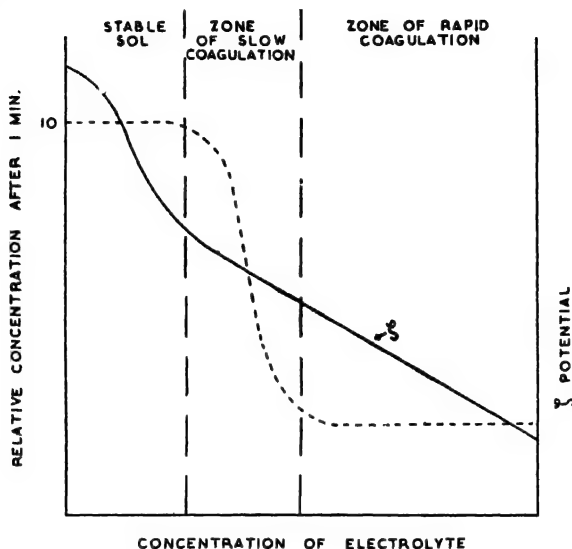
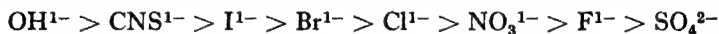
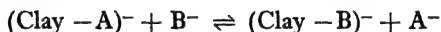


FIG. VIII.7. THE RELATIONSHIP BETWEEN THE ZETA-POTENTIAL AND THE EASE OF FLOCCULATION OF A KAOLINITE SUSPENSION (after Tuorila)

The Effect of Anions in Colloidal Suspensions. When other anions are introduced into a colloidal system, there will be a tendency for them to be adsorbed by the clay particles provided they are in excess. Particles which are capable of negative adsorption, preferentially select different anions according to the Hofmeister series.



However, the ionic exchange is an equilibrium process which may be represented quite generally as:



where A and B are any two different anions. Thus, if B is in excess the reaction will proceed to the right and the anion will replace, although the amount of replacement will be determined by the position of the anion in the Hofmeister series and its concentration.

Under certain conditions, therefore, other anions may preferentially replace hydroxyl units on the surface of clay particles. The effect of such replacements depends on the ionic size for, if the dimensions of the anion are large, a relatively

¹ Hauser, E. A. and Reed, C. E., *J. Phys. Chem. N. Y.*, 41, 911, 1937.

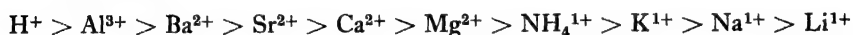
small number will be able to surround the particle. Consequently e (i.e. the charge on the particle) will be reduced, the number of counter-cations which are able to approach the surface will be less, hence d will also be reduced in the equation for zeta-potential. Although the dielectric constant D may be reduced also, the usual effect of adding an anion in the form of an acidic radicle to a clay suspension is to reduce the zeta-potential and increase the rate and amount of flocculation.

The Effect of Cations in Colloidal Suspensions. By virtue of their negative surface charge, clay particles have the capacity to attract and adsorb positively-charged ions (cations) from the surrounding suspension. These cations are not firmly held and under certain conditions they can readily be substituted by others. This property is known as the *base or cation exchange capacity* of the clay, and methods whereby it may be measured are described in Chapter V.

The addition of cations to a colloidal clay suspended in water has a pronounced and important effect. Most cations are larger and more readily hydrated than hydrogen ions, therefore if they are the counter ions in the clay micelle, the hydrated layer will be larger and the diffuse double layer increased as a consequence. The surface layers of the particles are capable of attracting a certain charge, hence it follows that more monovalent cations can be influenced than divalent ones, which in turn will be more numerous than trivalent cations. Also, the larger the cation and the greater its degree of hydration, the more molecules of suspension medium are likely to be influenced and oriented; hence the more extensive will be the diffuse double layer and the repulsive force which is exerted by a particle on other particles in the immediate vicinity will be increased and will operate and be effective through a much greater distance.

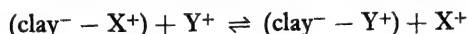
The tendency of the different cations to be adsorbed is again predicted by a Hofmeister series. In general the greater the charge and the higher the atomic weight of the cation, the more readily will it be adsorbed, although hydrogen ion (H^+) takes preference over all others.

The series is:



Therefore cations which would be valuable in increasing the zeta-potential and the degree of dispersion in a colloidal system are less readily adsorbed into the hydrosphere of the micelle.

This difficulty can be surmounted by adding an excess of the required cation because the replacement reaction is an equilibrium process thus:



where X^+ and Y^+ are any two different cations. Thus a sodium clay can be produced from a calcium clay by adding a sufficient excess of sodium ion and the amount of replacement is enhanced if at the same time the calcium ions can be removed from the system.

Monovalent cations such as potassium and sodium are large and highly hydrolysed. For a given charge on the adsorbing surface many more cations of this type can be attracted than (say) aluminium (Al^{3+}). For this reason and also because the number of oriented water molecules is much greater, the hydrosphere of particles

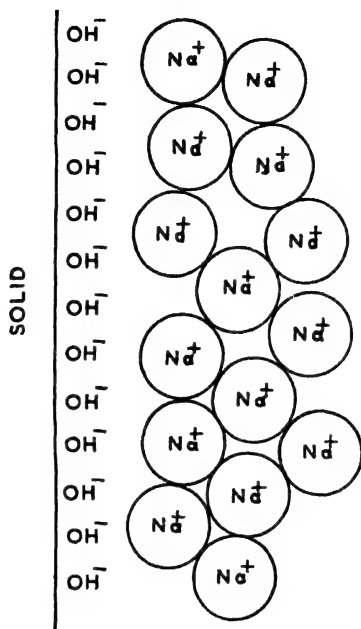


FIG. VIII.8. THE DIFFUSE DOUBLE LAYER WHEN SODIUM IONS ARE THE COUNTER-BALANCING CATIONS

with sodium or potassium as the counter-cations is extremely large. The zeta-potential of clays in this state is comparatively very large (Fig. VIII.8) and, consequently, the force of repulsion between particles is such as to produce maximum separation, or, in other words, a *deflocculated* system.

Clays which contain sodium or potassium as the counter ions in the colloidal micelle are, therefore, superior to all others in the production of a disperse or deflocculated system. This is shown by Fig. VIII.9 where the zeta-potential is plotted as a function of increasing electrolyte. As the zeta-potential may be regarded as a measure of the degree of deflocculation, the relative effectiveness of uni-, di- and trivalent cations may be directly compared.¹

At high concentrations of electrolyte or cation concentration the zeta-potential decreases because if the number of cations is increased excessively, they 'crowd' into the diffuse double layer, with the result that the field of influence of the negatively-charged surface is diminished, as shown in Fig. VIII.10. The thickness of the double layer (d) is reduced and, in the limiting case, cations may invade the surface layer itself and so reduce the surface charge (e). The reduction in zeta-potential which results, produces a lower degree of dispersion or deflocculation and will eventually cause coagulation.

The production of a deflocculated system or sol with univalent cations of sodium or potassium from a clay originally saturated with other cations is not an

¹ Phelps, G. W., *Ceram. Age*, 49, 162, 1947.

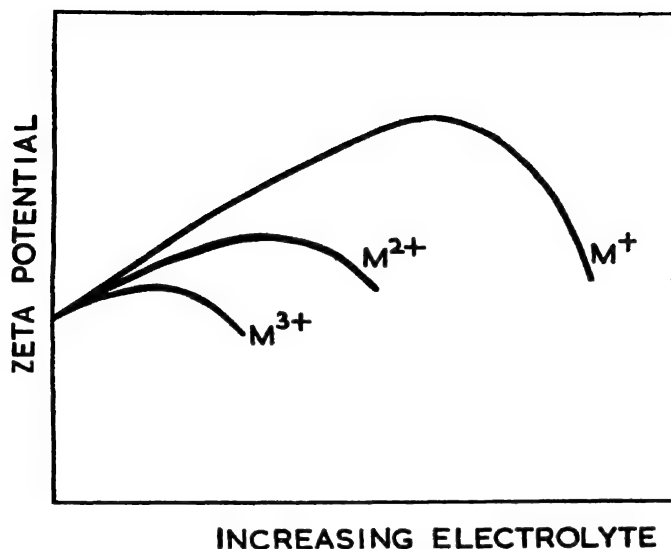


FIG. VIII.9. THE INFLUENCE OF CATIONS OF DIFFERENT VALENCIES ON THE ZETA-POTENTIAL

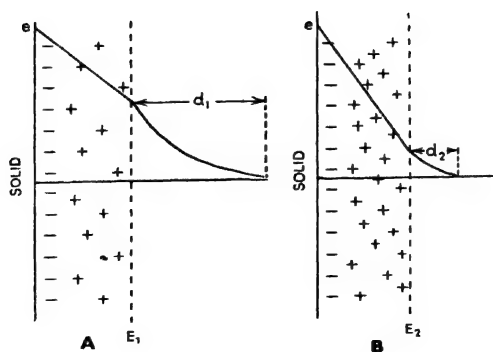
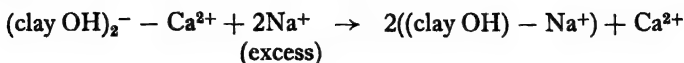


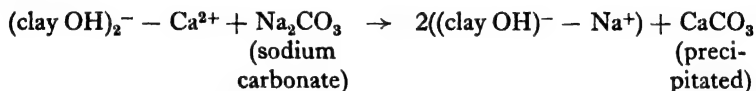
FIG. VIII.10. SCHEMATIC REPRESENTATION OF THE CROWDING OF THE DOUBLE LAYER BY AN EXCESS OF CATIONS

easy matter for, as has been shown, the former type of cations are less readily adsorbed. Provided sufficient univalent cations are present, however, the equilibrium system can be made to proceed to the right thus:



Although the production of a sodium clay is possible by such treatment, the excessive concentration of cations required may result in an overall reduction of the zeta-potential and caustic soda (NaOH) is not always effective in deflocculating a clay.

An alternative method for shifting the above equilibrium state to the right is to remove the calcium ions from the system by adding an anionic component which causes precipitation of an insoluble calcium salt. Carbonate, silicate and phosphate radicles are effective for each forms a calcium salt of low solubility. The reaction then proceeds:



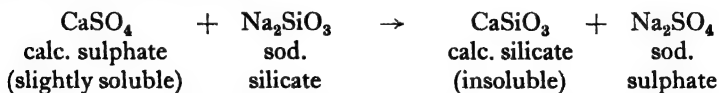
Only small amounts of the sodium salt are required—sufficient to cause the precipitation of the total calcium content of the clay.

In the more general case of a clay saturated with any cation, the most effective precipitant is the phosphate radicle which forms insoluble salts with most cations. Sodium hexametaphosphate is, for this reason, widely used as a deflocculating agent for clays, but its mode of action involves more than simple ion exchange.

The effects of increasing the deflocculation of clay are to decrease the apparent viscosity (which increases the ease of flow), and to stabilise the suspension.

The relative effect of sodium hydroxide and sodium silicate on the deflocculation of a clay is shown in Fig. VIII.11. The influence of each on the viscosity of a 16 per cent kaolinite suspension previously saturated with calcium ions is clearly demonstrated.

As Holdridge¹ has pointed out, the presence of additional salts in a clay may produce abnormal behaviour when electrolytes are added. He cites the case where sodium silicates actually caused flocculation of a clay which was contaminated with calcium sulphate. A double decomposition between the electrolyte and the salt presumably took place with the formation of insoluble calcium silicate and highly soluble sodium sulphate thus:



As a result of such reactions free sulphate ions (SO_4^{2-}) are liberated into the dispersion medium and can to some extent replace hydroxyl ions in the double layer. The zeta-potential will be lowered with consequent flocculation. This is avoided by

¹ Holdridge, D. A., *Trans. Brit. Ceram. Soc.*, 49, 286, 1950.

the prior addition of a little barium hydroxide ($\text{Ba}(\text{OH})_2$) to precipitate the sulphate radicle as insoluble barium sulphate.

Anomalous flocculation also occurs when a mixture of caustic soda and sodium chloride is added to a hydrogen clay. Increasing additions of this mixture will cause first a flocculation, then dispersion and finally a second flocculation or coagulation. The first flocculation is due to the invasion of the hydrospheres of the clay micelles by chloride ions which replace the hydroxyl units, thereby reducing the zeta-

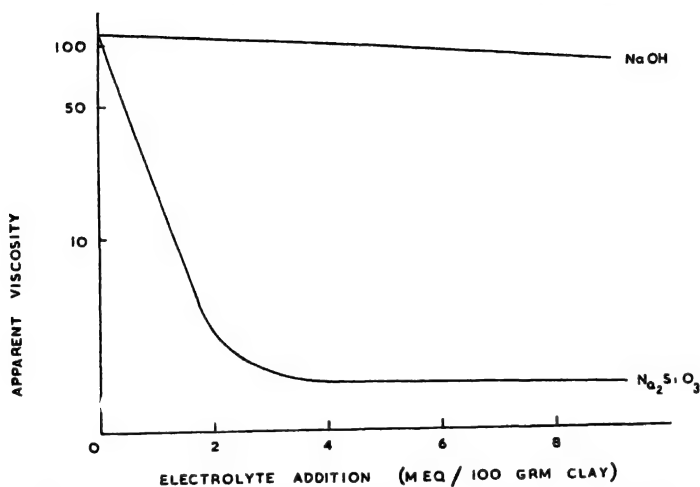


FIG. VIII.11. THE INFLUENCE OF SODIUM HYDROXIDE AND SODIUM SILICATE ON THE DEFLOCCULATION OF A CALCIUM CLAY

potential and causing flocculation. As the concentration of sodium ions from the sodium hydroxide is increased, the zeta-potential is raised and deflocculation occurs. Finally at high concentrations, excess sodium ions reduce the thickness of the double layer and the surface charge of the clay particle and so the final coagulated state is formed. This is illustrated graphically by Fig. VIII.12, where the degree of dispersion is judged from the amount of clay remaining in suspension after one hour.

Flocculation or the reduction in zeta-potential may also be caused by adding a colloid of opposite electrical charge. Thus ferric hydroxide which is a positively-charged colloid will cause precipitation of the negative clay colloids. Stremme has suggested that some natural clays may have been produced by the mutual precipitation of colloidal alumina and silica, these substances bearing opposite charges and producing mixed gels. The derivation of the fuller's earth clays of Surrey and Bath may have been of this type.

The **conditions favouring deflocculation** are:

- The presence of monovalent cations which are capable of being heavily hydrated.
- The elimination of other cations preferably as insoluble salts.
- An excess supply of free hydroxyl units (OH^-) in the dispersion medium.

(d) The removal of other anions which tend to replace hydroxyl units in the double layer.

(e) Not too great an excess of electrolyte in the dispersion medium, which is usually controlled by maintaining the P_H between 10–12 depending on the type of electrolyte used.

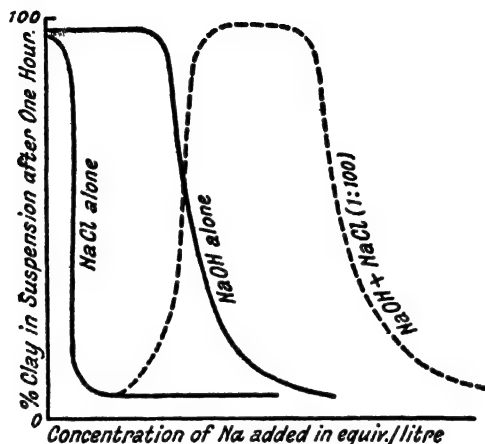


FIG. VIII.12. ABNORMAL FLOCCULATION OF CLAY (Oakley)

Protective colloids have the effect of stabilising a clay suspension and preventing or restricting flocculation. Probably the best natural examples of protective colloids are the humus compounds in soils and colloidal lignite in ball clays. Hauser has suggested that humus, lignin and similar materials contain large-sized cations which take part in the double layer and prevent the entry of deleterious ions. The same effect can be produced artificially by adding suitable substances to the clay. Thus crushed lignite is often incorporated into casting slips and the salts of large-sized organic cations are being used extensively to improve the qualities of soils. The value of sodium hexametaphosphate as a deflocculant is thought to be due to its capacity to form a protective colloid.

The concept of zeta-potential is valuable for explaining many of the unusual features of slip formation and casting properties and many of the physical phenomena associated with these systems may be readily explained by considering the principles outlined in the previous pages.

Amongst these are the following:

(a) **Thixotropy.** It is well known that when a suspension of certain clays is charged with electrolytes, the system on standing appears to *set* and to have many of the characteristics of a *gel*. This state can readily be destroyed by shaking or stirring the material, when immediately a free-flowing liquid *sol* is restored. If the disturbing influence is removed the gelation reappears. To describe this phenomenon the word *thixotropy* is used; it is derived from the Greek *thixis*—the touch, and *trope*—a change.

Freundlich has studied this interesting phenomenon in detail and enumerated many of the contributing factors. Along with other co-workers,¹ he discovered that alkali ions were an essential requirement in the production of a thixotropic suspension of montmorillonite; a dialysed clay (i.e. hydrogen), showed no tendency to gel. Hauser¹ has shown that although there is little or no volume change when thixotropic gels form, all Brownian Movement stops even when the particle size is extremely small indicating that a structure of some type must be formed in which the clay particles, the excess cations and the dispersion medium itself must all play some part. He concludes that the colloidal micelles are locked in an equilibrium position in a type of balanced electrical lattice, where cations in the medium maintain the negative clay particles at a certain separation distance. There is almost certainly a high degree of induced particle orientation which if disturbed will destroy the thixotropic nature—a point beautifully demonstrated by Hofmann, Fahn and Weiss.²

Thixotropy may be regarded as a half-way state in the process of coagulation. The addition of more electrolyte to a thixotropic system causes more cations to 'crowd' into the colloidal micelle, with a consequent reduction in the zeta-potential. A coagulated gel is, for this reason, of an entirely different origin from a flocculated one, and although these are often confused they are entirely different in character. A flocculated system will sediment rapidly usually to a small volume; but coagulated particles settle slowly and invariably form a bulky deposit which is troublesome when casting ware.

(b) **Rheopexy.** Rheopexy is closely allied to thixotropy and although the term is not strictly accurate it has been called 'induced thixotropy'. The thixotropic gelation of some suspensions may be slow to develop especially when the particles present are rather large (0.03 microns). If, however, the suspension is vibrated gently or subjected to some other rhythmical movement, gel formation may be produced much more rapidly. Hauser and Reed³ have demonstrated that in certain montmorillonite sols where normal thixotropy was not obvious in 100 minutes, an effective gel could be induced in less than a minute by vibrating the suspension. Rheoplectic behaviour is not general in all suspensions which exhibit thixotropy, but where the particle shape is such that orientation can be developed as a result of vibration, rheopexy will be at a maximum. This is particularly so in the case of clays where the plate-like particles are readily aligned parallel to their basal section on the application of slight forces.

The importance of rheopexy in ceramic suspensions cannot be over-estimated for many of the problems in slip casting may be related to this phenomenon. Some clay slips show little thixotropic behaviour under normal conditions, but, when they are cast in plaster-moulds, the draining effect may cause orientation and rheopexy. As a result an undesirable low-density body will be formed. Rheopexy may also be induced during the extrusion of plastic clays.

(c) **Dilatency.** Almost directly opposed to thixotropy in effect is *dilatency*, which is exhibited so readily by sand and other substances where the grain size of particles present is comparatively large.

¹ Hauser, E. A., *J. Amer. Ceram. Soc.*, **25**, 233, 1942.

² Hofmann, U., Fahn, R. and Weiss, A., *Clay Min. Bull.*, **10**, 70, 1953.

³ Hauser, E. A. and Reed, C. E., *J. Phys. Chem.*, **41**, 911, 1937.

The phenomenon will be known to all who have walked on a sandy beach near to the water's edge as the tide is ebbing. Sand, which is apparently wet and moist, will become dry immediately pressure is applied to it; in other words, an apparently liquid suspension becomes solid when stirred or agitated.

Dilatancy is particularly troublesome when finely-grained powders of non-plastic materials are being made up into slips or suspensions. These tend to adsorb small amounts of water and any attempts to stir or agitate the mixture are opposed by the dilatent effect. Whereas thixotropic systems are readily broken down by an applied force, dilatent suspensions form a more rigid and retentive structure. When the pressure is removed the system returns to its former state.

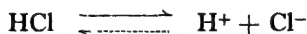
The earliest explanation of the phenomenon of dilatancy was attempted by Reynolds¹ in 1886 and his views are still generally accepted. When particles of wet sand are closely packed there is a certain amount of void space. If pressure is applied to this mass, the closeness of packing will be destroyed and a larger volume of voids and interstices will form into which any surplus liquid can penetrate. Because the hydrosphere around each individual grain is reduced the mass becomes hard and dry and will not flow with the same ease as before.

(d) **The Acidic Nature of Clay Suspensions.** Because hydrogen ions are preferentially absorbed by clay particles, most natural clays contain hydrogen, in part at least, as their exchangeable cation (see p. 267). Consequently, when such clays are suspended in water, dissociation occurs and the hydrogen ion concentration in the suspension is increased.

The acidity of a solution is defined in terms of the dissociated hydrogen ions which are present. In pure water the amount of dissociation of the molecule, H_2O , into the ions, hydrogen (H^+) and hydroxyl (OH^-) is small and only 10^{-7} gram-molecules of hydrogen ion per litre are present. The equilibrium in water can be written

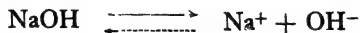


If an acid is added to water the content of free hydrogen ions is increased in proportion to the amount of acid added and to the degree to which it is dissociated. A strong acid is defined as one in which the degree of dissociation is very great; hydrochloric and nitric acids are almost entirely ionised thus:



Some acids, e.g. acetic, are feebly ionised, and in equivalent concentrations yield far less hydrogen ions than strong acids.

Basic substances are those which form solutions of lower hydrogen ion concentration than pure water. Their mode of action may be simply conceived, by visualising the base dissociating into a cation and hydroxyl ions thus:



When the base is dissolved in water, the concentration of hydroxyl ions in solution is increased above that normally found in pure water. Consequently by

¹ Reynolds, O., *Nature*, 33, 429, 1886.

the Law of Mass Action, the concentration of hydrogen ions will be reduced below that found in pure water.

The hydrogen ion concentration is defined as the number of gram-ions of hydrogen in a litre of solution. As this amount is extremely small it is usually expressed as the logarithm of its reciprocal which is known as the pH value. The number of gram-ions of hydrogen in pure water is 1×10^{-7} ; hence its P_H is 7.

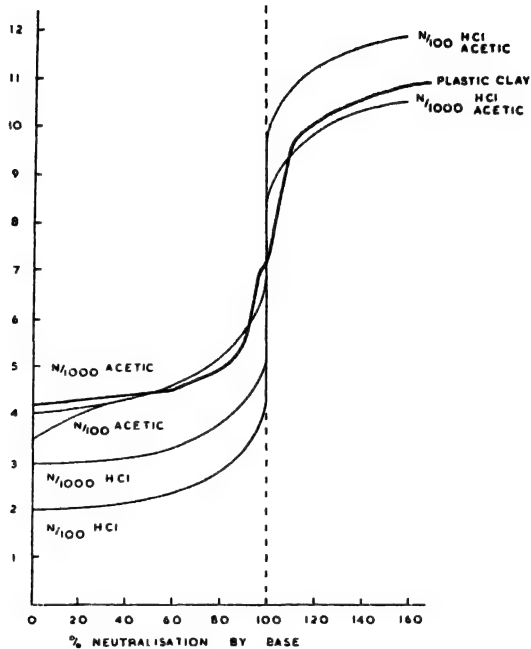


FIG. VIII.13. THE ACIDIC NATURE OF CLAY SUSPENSIONS

As all the solutions with a pH less than 7 are acids (i.e. have an excess of hydrogen ion) and all with a pH greater than 7 are alkaline (i.e. are deficient in hydrogen ion) the pH is a means of assessing the acidity or alkalinity of a liquid.

The pH value of most clay suspensions lies between 4.2 and 7.0 indicating that they behave as weak acids.

This is borne out by titration curves of clay suspensions with bases; the pH changes in a manner comparable to that of a weak acid (Fig. VIII.13).

Many clays, however, owe their acidity not only to the exchangeable hydrogen ions which they have absorbed but to associated organic matter. Humic and other soil acids are frequently associated with clays as 'protective colloids' and these, even in small amounts, may produce marked acidity in clay suspensions.

(e) **Plasticity.** Probably the most important aspect of clay/water systems is the *plasticity* or resistance to flow of suspensions when the concentration of solid matter becomes appreciable. Plasticity is in some ways related to the viscosity of the clay/

water system or in other words the resistance to flow which is set up in a suspension. The factors, therefore, which influence the apparent viscosity of a liquid as the concentration of suspended matter is increased, may be studied with advantage before considering the fundamental property of plasticity.

VISCOSITY AND RHEOLOGY

THE viscosity of a liquid is an indication of its ease of flow. In ideal cases, the rate of flow depends only on the pressure or force applied to cause it to flow.

The term *rheological properties* (devised by Bingham in 1928) is used to indicate all properties relating to the flow of all pastes and non-ideal liquids. It is specially important in connection with the flow of slips and the behaviour of clay-pastes, but it may be extended to include the partial flow of clays, etc., when in a kiln.

Plastic clays are exceptional in requiring a double graph to describe their flow under pressure and because the amount of deformation is roughly proportional to the *rate* at which the shear or pressure is applied.

As the concentration of a clay suspension increases, its properties change from true viscous flow to plastic flow. The character of the clay/water mixtures changes from suspensions and slips, through pastes and muds, to plastic masses which are deformed only by high pressures.

SUSPENSIONS AND SLIPS

As the limiting case, the viscosity relationships in a liquid free from any suspended material must be considered. The **viscosity of a liquid** is defined as the ratio between the force applied to a liquid and the shearing stress which is produced, and represents the resistance of a fluid to change of shape or motion. This is more clearly appreciated by considering a simple type of viscometer (Couette design) illustrated in Fig. VIII.14. A fluid is placed in the space between two co-axial cylinders C_1 and C_2 . The internal cylinder can be rotated at different velocities and, in order to keep the outer one C_2 at rest, a tangential force F has to be applied.

The viscosity is related to the ratio of F (the shearing force applied) to v the velocity of rotation (which is related to the shearing rate).

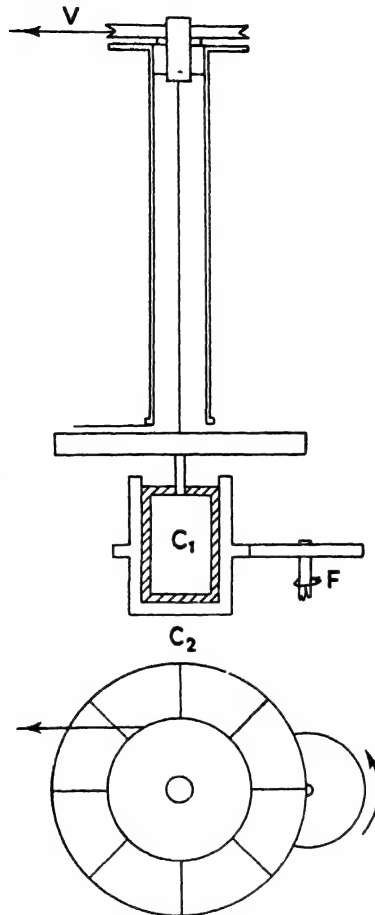
The complete expression for an ideal liquid is

$$F = kA_d \frac{v}{d}$$

where A is the interfacial area of the rotating cylinder, d is the separation between the cylinders and k is a constant. If v/d and A are reduced to unity then $k = F = \eta$, i.e. the coefficient of viscosity.

The *unit of viscosity* is defined (in c.g.s. units) as the number of dynes per sq. cm. required to maintain a velocity of 1 cm. per sec. between two surfaces, each of 1 sq. cm. area and 1 cm. apart and is termed a *poise* which is represented by η . As the poise is often inconveniently large the *centipoise* ($\eta \times 10^{-2}$) and the *millipoise* ($\eta \times 10^{-3}$) are frequently used. Thus, water has a viscosity of about 1 centipoise and glycerine about 10 poises.

FIG. VIII.14.
PRINCIPLE OF THE
COUETTE VISCOMETER



Viscosity is also stated in terms of *stokes* or *centistokes*; this is the unit of kinematic viscosity and the poise the unit of dynamic viscosity. The viscosity in stokes can be found by dividing the viscosity in poises by the specific gravity of the liquid.

The physical concept of viscosity is the frictional resistance of molecules of the liquid to the movement of similar molecules in their immediate vicinity. It is occasionally expressed as a reciprocal or $1/\eta$ when it is known as the *fluidity*.

The viscosity of a liquid or fluid is a direct measure of the ease of flow; hence it is an important and often critical value of clay suspensions and casting slips. It is measured by means of a *viscometer*.

These are of many designs¹ although those of importance in ceramic practice are of four groups.

¹ Philippoff (see p. 455) has described almost 200 different types of viscometers and subdivides them into eight groups.

A. Rotating Cylinder Viscometer. The principles of the method have already been introduced in the previous section where the well-known Couette viscometer (Fig. VIII.14) was illustrated. Several other designs embody these same principles with but minor embellishments. Most modern instruments of this type are designed so that the outer cylinder rotates and the shearing stress on the internal one is measured by observing the angular twist on a fibre or spring suspension. The shearing force can be varied by changing the speed of rotation of the outer cylinder or the space between the two.

The complete expression relating the viscosity of a liquid with the angular twist and the velocity of rotation of the cylinder, depends also on the characteristics of the torsion wire. Normally in a commercially-manufactured instrument of the type illustrated in Fig. VIII.15 the makers supply a list of correction factors to relate the angular twist to the apparent viscosity under a particular set of conditions. Clark and Hodsman¹ have derived a mathematical expression of general application to all rotating cylinder viscometers.

The viscometer illustrated in Fig. VIII.15 is a portable instrument which is very serviceable for the routine control of slips. The reading on the dial can be directly converted to the apparent viscosity and it is also possible by its use to measure the thixotropic behaviour of a slip.

B. Flow of Liquid in a Tube. A useful method of assessing the viscosity of slips is to measure the rate of flow of liquid in a tube when subjected to a certain pressure head. If the bore of the tube is known, the time taken for a given volume to pass a certain point may be calculated and hence the rate of flow determined.

Viscometers of this type are based on an original method by Ostwald,² whose apparatus is shown in Fig. VIII.16A. The slip or suspension is poured into the left-hand limb of the U-tube, which has a narrow capillary section along part of its length. Under standardised conditions, the time taken for a constant volume of liquid to flow through the capillary section is related to its viscosity. The usual practice is to measure the time taken for the level of liquid in the tube to fall between two arbitrary marks R_1 and R_2 and to calibrate the apparatus with liquids of known viscosity.

C. Falling Sphere Viscometer. A simple, but nevertheless effective type of viscometer involves measuring the rate of fall of a sphere of known dimensions when it is allowed to fall freely in a column of the liquid.

Although under carefully controlled conditions of experiment the viscosity of the liquid can be theoretically predicted from Stokes's Law (see p. 381) provided that the velocity of fall and the diameter and density of the sphere are measured, correction factors have to be applied in practice. These are necessary because the sphere has to be sufficiently large to enable it to be seen and consequently its fall is not streamlined. Because of these drawbacks, the falling sphere viscometer is more commonly used after being calibrated with liquids of known viscosity.

A small steel ball (S) is allowed to fall in a cylinder (Fig. VIII.16B) containing a liquid of known viscosity (η_1) and known specific gravity (ρ_1); the time (t_1) taken for it to fall between two marks (R_1 and R_2) is noted. The same test is repeated with the

¹ Clark, A. A. and Hodsman, H. J., *J. Soc. Chem. Ind.*, 56, 67, 1937.

² Ostwald, W., *Kolloid Zeit.*, 12, 213, 1913.

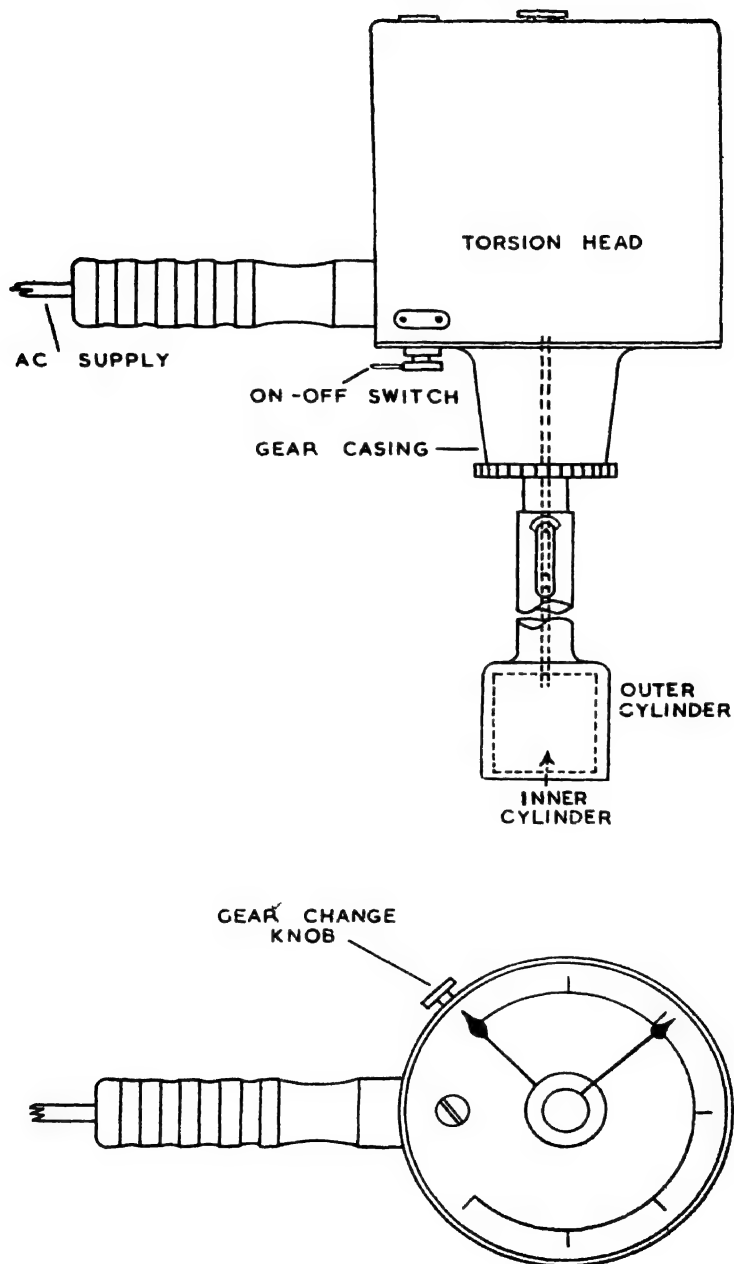


FIG. VIII.15. A PORTABLE ROTATING CYLINDER VISCOMETER
(Supplied by Ferranti Ltd.)

liquid or suspension, the viscosity of which is to be measured, and the time of fall (t_2) between the same two marks again noted. If the specific gravity of the test liquid is ρ_2 , the following relationship can be applied to determine its viscosity (η_2):

$$\frac{\eta_1}{\eta_2} = \frac{t_1}{t_2} \frac{(\rho - \rho_1)}{(\rho - \rho_2)}$$

where ρ is the specific gravity of the steel ball.

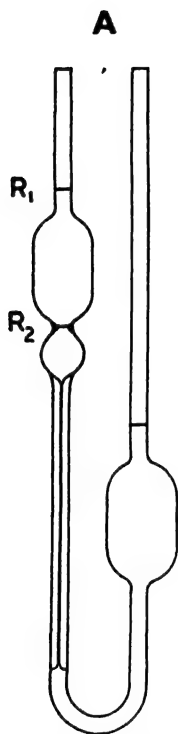


FIG. VIII.16A.
THE OSTWALD
VISCOMETER

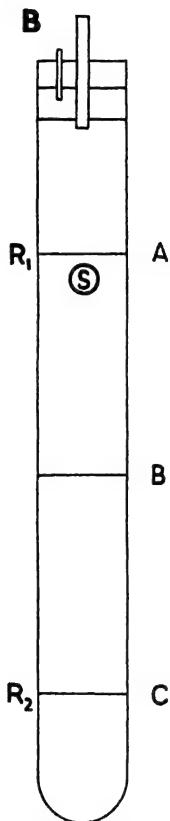


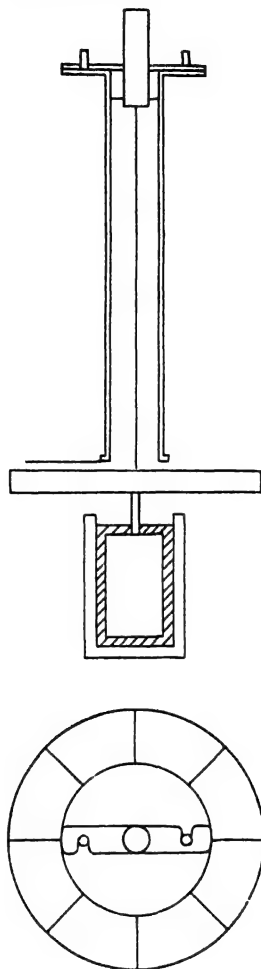
FIG. VIII.16B.
THE FALLING
SPHERE VISCOMETER

This method is liable to error if the particles in suspension settle appreciably during the time taken for the test. The falling sphere viscometer is most effective when the viscosity of the fluid being tested is high, and when it is non-opaque.

D. Torsion Viscometers (Fig. VIII.17) have been used for determining the viscosity of clay suspensions (slips) since 1908 in which year A. V. Bleininger¹ immersed a heavy horizontal disc or cylinder suspended by a long wire in a tank

¹ Bleininger, A. V., *Trans. Amer. Ceram. Soc.*, 10, 389, 1908.

FIG. VIII.17.
THE TORSION VISCOMETER



containing a clay slip, turned it through an angle of 180° , released it and measured the amplitude of the swings several times. At a fixed temperature, the ratio between two consecutive amplitudes of swing is constant for a given slip and the relative viscosity (η) can be calculated from the equation:

$$\eta = \frac{t_2 \log r_1}{t_1 \log r_2}$$

where t_1 and t_2 are the periods of oscillation in water and the slip respectively, whilst r_1 and r_2 are the ratios of the amplitudes of any two consecutive swings in the same direction in the same liquid at the same temperature. Numerous modifications have been made in the design of torsion viscometers, but the principle of all is the same.

An apparatus developed by Norton¹ is relatively simple to construct and is widely employed in the ceramic industries.

The Couette and torsion viscometers are the most commonly used in the ceramic industries because of their convenience and because they do enable a reasonable amount of control over the properties of slips to be exercised. It should never be forgotten, however, that the property of viscosity as applied to suspensions is so complex and its measurement involves so many factors that no single figure can accurately represent it.

THE FLOW PROPERTIES OF LIQUIDS AND SUSPENSIONS

WHEN an ideal liquid is being tested, the ratio of the shearing rate to the shearing strain is constant and independent of the force applied. In other words the viscosity of such a liquid is constant at all rates of shear, so that its coefficient can be assessed from the slope of a graph of shearing rate against shearing strain. This type of behaviour is known as *Newtonian flow* and it is illustrated in Fig. VIII.18A.

This is rarely, if ever, attained in practice, because in an ideal liquid the molecules are capable of streamlined flow. For all practical purposes, however, water and other simple organic liquids may be so regarded for their coefficient of viscosity is sensibly constant except at extremely high shearing rates.

If a small concentration of spherical particles is added to a liquid the coefficient of viscosity is increased, although the suspension may still behave as though it were an ideal liquid. The ratio of the shearing rate to the strain imposed still remains sensibly constant at all values thereby implying that the viscosity is independent of the applied force.

As the concentration of particles is increased however the flow properties of the suspension depart from those in ideal *Newtonian flow*. As the shearing rate is increased, the strain imposed does not increase linearly. The coefficient of viscosity increases with the applied force. This is expressed graphically in Figs. VIII.18A and B. The former shows the variation of shear rate with strain for an ideal liquid and the latter for a suspension; Fig. VIII.19 indicates the variation in apparent viscosity with the shearing rate and demonstrates the deviation from ideal conditions as the concentration of the suspension is increased.

When non-spherical particles, e.g. clay minerals, are added to the liquid phase, the deviation from Newtonian flow is more pronounced than when all the particles are true spheres. This is due to the fact that when a driving force is applied to a suspension the rate of flow induced is influenced by the following:

- (a) The resistance of the molecules of the medium itself.
- (b) The presence of particles in the medium which have to be moved along with the liquid. Not only is there a translatory movement involved but when the particles are irregularly shaped there may be rotational movement in the velocity-gradient of the sheared liquid.
- (c) At high concentrations, the particles may be sufficiently close to permit

¹ Norton, F. H., *J. Amer. Ceram. Soc.*, 21, 33, 1938.

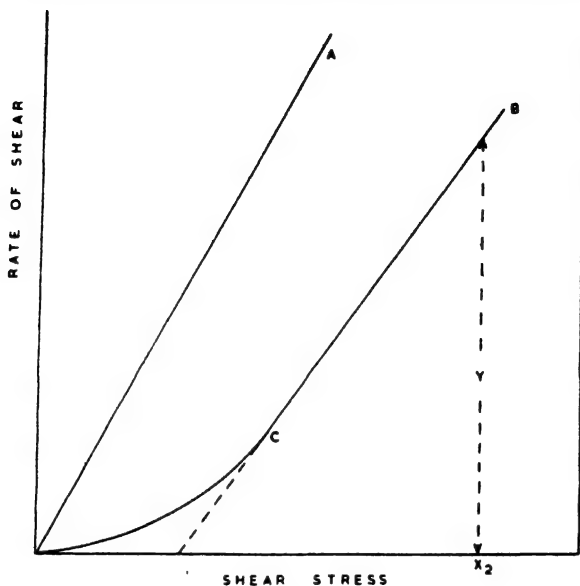


FIG. VIII.18.

(A) NEWTONIAN, AND (B) NON-NEWTONIAN FLOW

In the former, the slope of the stress/strain line, i.e. the viscosity, is constant at all stress values, but in the latter, the relationship is non-linear. The apparent viscosity in non-Newtonian flow is given by X_1/Y and will decrease with increasing stress. The value X_1 which is the extrapolation of BC to zero strain is sometimes called the Yield Value

mutual interference of their electrical fields. Consequently there will be serious resistance to flow.

For these reasons, the rate of flow of a suspension becomes progressively more restricted as the concentration of solid matter is increased. Furthermore, the amount of restriction depends on the velocity of flow, i.e. the shearing rate, and a linear relation between this factor and the strain imposed does not hold (Fig. VIII.18B). Whenever the viscosities of suspensions have to be compared, it is vitally important to carry out all tests under the same conditions of shearing rate. The value so determined is termed the *apparent viscosity* and the conditions under which it is measured should always be stated.

According to Philippoff¹ many factors contribute to the apparent viscosity of a suspension and it is not an easy matter to investigate the influence of one whilst maintaining the others constant. These include:

- (a) The concentration of suspended material.
- (b) The size of particles, their distribution and the degree of dispersion.
- (c) The shape of particles.

¹ Philippoff, W., *Viskosität der Kolloide* (Steinkopff, Dresden and Leipzig, 1942).

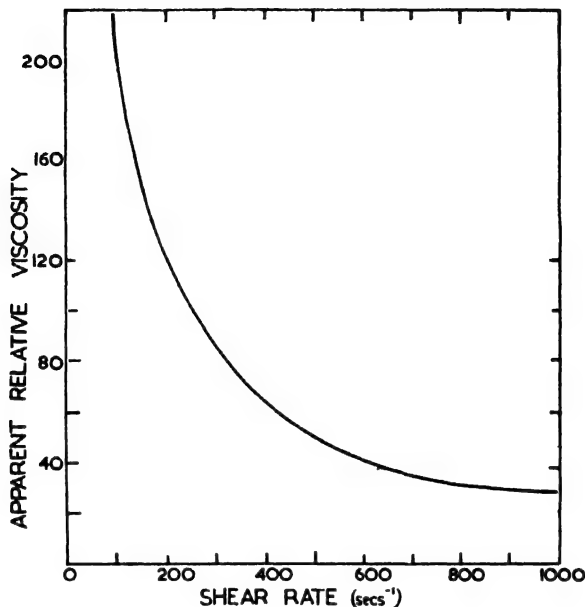


FIG. VIII.19. THE VARIATION OF THE APPARENT VISCOSITY OF A CLAY SUSPENSION WITH INCREASING SHEAR RATE

- (d) The electrolyte type and concentration, or, in other words the zeta-potential.
- (e) The flexibility or deformability of the colloidal micelles in the suspension medium.
- (f) Anomalous behaviour, e.g. thixotropy, rheopexy, dilatency, etc.
- (g) The temperature of the suspension.

The **dependence of viscosity on the concentration of particles** has been intensively studied and many writers have evolved mathematical relationships to describe particular systems. It is however only with very dilute suspensions that a general relationship can be applied. The *Einstein equation*¹ holds when the concentration is very low, so that the suspended particles present are widely separated and their electrical fields do not interfere. Viscosity is then a linear function of the *volume* concentration of particles and may be expressed as

$$\eta_a = \eta_m(1 + k\phi)$$

where η_a and η_m are respectively the observed viscosity and the viscosity of the suspension medium, ϕ is the volume concentration (expressed as a fraction) and k is a constant which for spherical particles has the value 2.5.

Smoluchowski² arrived at a similar conclusion but others have suggested that

¹ Einstein, A., *Ann. Physik.*, 19, 301, 1906 and 34, 592, 1911.

² Smoluchowski, M., *Kolloid Zeit.*, 18, 190, 1916.

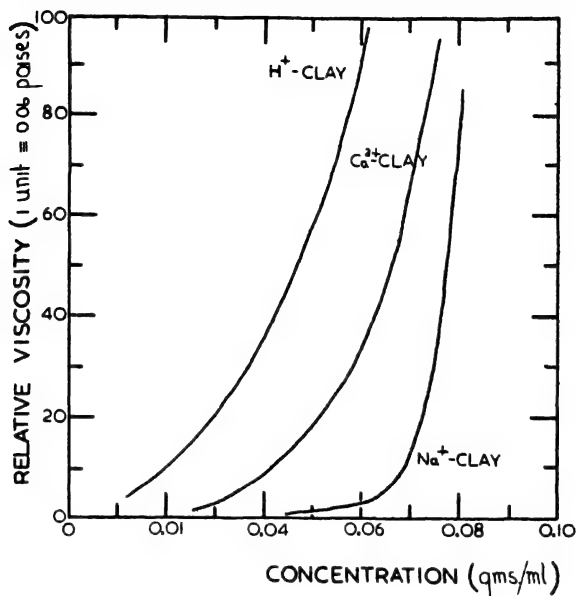


FIG. VIII.20. THE EFFECT OF THE CONCENTRATION OF A CLAY SUSPENSION ON THE APPARENT VISCOSITY
The effect of different saturating cations is also shown

the value of the constant may be higher, particularly when particles of less symmetrical shapes are considered.

This equation applies only at extremely small concentrations, in fact, clay suspensions with more than 2 per cent of solid matter may show considerable deviation. The mutual interference of particles becomes the predominating influence at higher concentrations and as Fig. VIII.20 shows, above a certain critical concentration the rate of increase in viscosity with concentration is extremely rapid.

Norton has suggested that this critical point in the viscosity curve is related to the concentration at which the particles are so close that free rotation is impossible. In other words, when the calculated separation distance of particles becomes less than the size of the particles present, the apparent viscosity of the system is greatly increased. These conclusions have been confirmed by experiments on fractionated clay suspensions where the particles are all of one size, but the influence of the electrical field around particles cannot be ignored, and the size of the colloidal micelles is probably of paramount importance.

The mathematical treatment of the viscosity/concentration relationship at high concentrations is far from established and many different equations have been advanced. Some writers have simply introduced an additional term into the Einstein equation, which would be the predominating influence when the amount of suspended material was large, thus:

$$\eta_a = \eta_m(1 + k_1\phi + k_2\phi^n)$$

Norton, *et al.*,¹ for example, applied such an equation in studies on mono-dispersed kaolinite suspensions and found that in a flocculated system n was near to 3 whilst with clay in the deflocculated state n approximated to 12.

A more general form of the equation has been suggested by Baker² as follows:

$$\eta_a = \eta_m(1 + k\varphi)^n$$

On this basis the equation of Norton would be correct to a first approximation. Similarly, if φ were very small, the equation would simplify to the Einstein form.

Mooney³ has predicted from theoretical reasoning that the viscosity of a suspension of spherical particles should obey the following equation

$$\eta_{rel} = \text{exponential} \frac{(a\varphi)}{(1 - k\varphi)}$$

where η_{rel} is the apparent viscosity relative to that of the medium, φ the volume concentration of particles and a and k are constants, the former depending on the shape of the particle and the latter on the 'crowding' or packing. To a first approximation and providing the concentration is not excessive this will simplify to

$$\text{ion } \eta_{rel} = \frac{a\varphi}{1 - k\varphi}$$

T. E. Currie⁴ has shown that this equation can be applied to deflocculated clays over a comparatively large range of concentration (up to 30 per cent by weight).

The **influence of grain size on the viscosity of clay suspensions** is most pronounced. The finer the particle size the greater will be the viscosity for a given slip concentration as Fig. VIII.21 shows. Undoubtedly the *surface area of the particles* in a suspension is a determining factor on the viscosity and, in this sense, the *particle shape* is an important contributor. Plate-like and fibrous particles have a larger surface factor than spheres or cubes and consequently the viscosity of such particles is larger for an equivalent concentration.

The **electrolyte type and concentration** have a great influence on the apparent viscosity of clay slips and suspensions and their behaviour is most probably related to the changes which they produce in the zeta-potential. The effect of adding an electrolyte to a suspension of a flocculated clay has been demonstrated by Henry and Taylor⁵ and their results are shown in Fig. VIII. 22. If a weak solution of sodium hydroxide is added to a suspension of a hydrogen clay, sodium ions progressively replace the hydrogen and increase the zeta-potential. Although the acidity of the suspension (as shown by changes in P_H) is gradually lowered, the change in the viscosity is small until the suspension becomes just basic when an amazing increase in fluidity takes place; the viscosity changes to about 1/200 of its original value. Further additions of alkali produce a more alkaline suspension, but the viscosity—which is not much different from that of the suspending medium—

¹ Norton, F. H., Johnson, A. L. and Lawrence, W. G., *J. Amer. Ceram. Soc.*, 27, 149, 1944.

² Baker, F., *J. Chem. Soc.*, London, 103, 1653, 1913.

³ Mooney, M., *J. Coll. Sci.*, 6, 164, 1951.

⁴ Currie, T. E., Leeds University Ph.D. thesis, 1954.

⁵ Henry, E. C. and Taylor, N. W., *J. Amer. Ceram. Soc.*, 21, 165, 1938.

does not change again until the amount of alkali added becomes excessive, when the cations invade the double layer and cause coagulation. According to Henry and Taylor the amount of alkali which is required to bring out the reduction in viscosity of the hydrogen clay is equivalent to its base exchange capacity (see p. 264). All clay suspensions are susceptible to changes in viscosity under conditions of varying electrolyte type and amount. The presence of monovalent cations, such as sodium

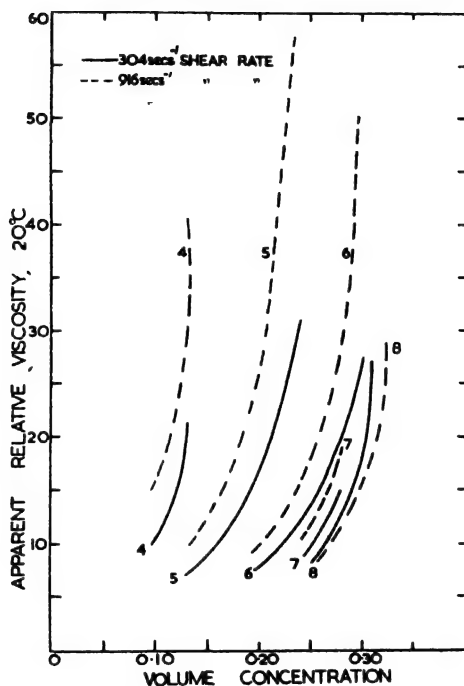


FIG. VIII.21. THE EFFECT OF PARTICLE-SIZE ON THE APPARENT VISCOSITY OF KAOLINITE SUSPENSIONS

Particle-ranges: (4) 0.15-0.20 μ ;
(5) 0.20-0.30 μ ; (6) 0.30-0.50 μ ;
(7) 0.50-1.0 μ ; (8) 1.0-2.0 μ .

The relationship at two rates of shear is shown

and potassium favours lower viscosities at a particular concentration than are given by di- and trivalent cations and also hydrogen ion. The viscous behaviour of kaolinite, montmorillonite and attapulgite clays are compared in Fig. VIII.23 which shows the viscosity/concentration relationship and the influence of sodium hexametaphosphate and hydrochloric acid additions on the natural clays.

The physical concepts of the behaviour of clay suspensions in the presence of electrolytes have not been completely explained. It has been suggested that electrolytes reduce the 'drag' or surface tension of the particles in water. This theory is supported to some extent by the fact that some camphorated products and

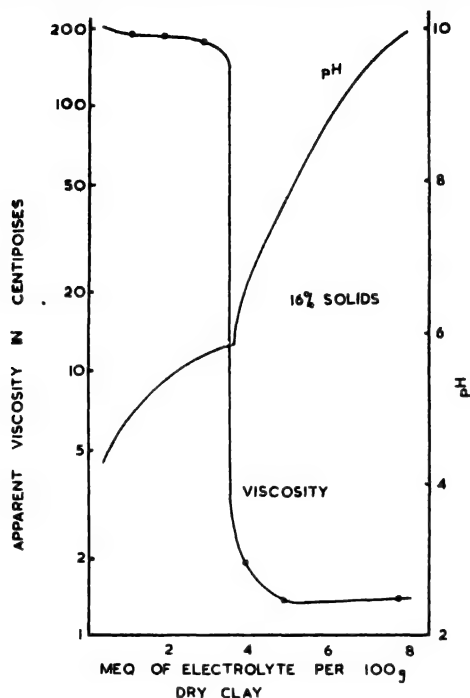


FIG. VIII.22. THE INFLUENCE OF ADDITIONS OF SODIUM HYDROXIDE SOLUTION ON THE APPARENT VISCOSITY OF A FLOCCULATED, HYDROGEN CLAY (after Henry and Taylor)

other detergents reduce the viscosity of clay suspensions without influencing the cation exchange. They may act, however, by forming *protective colloids* (see p. 444), so more is involved than a simple surface tension change in these cases. Norton¹ has suggested that in a flocculated system the individual particles are in an equilibrium position with respect to each other on account of the forces of attraction and repulsion. Flow under such conditions is possible only when force is applied to disturb the equilibrium disposition of the particles, so that the viscosity will be high. In deflocculated masses, Norton considers that there are no attractive forces between particles, so that they are easily disturbed and the suspension has a much lower viscosity.

Neither of these two theories to explain the behaviour of electrolytes on clay suspensions is generally accepted, but no suitable alternative has so far been advanced which accounts for all the known facts.

The **nature of the colloidal micelles** has an influence on the viscosity of suspensions, but there is little conclusive evidence on this point. The water molecules which are held by the clay particles are influenced both in their amount and the

¹ Norton, F. H., *Elements of Ceramics* (Addison-Wesley Press Inc., Cambridge, Mass., 1952).

rigidity of their bonding by associated cations. Weakly-held hydrospheres are easily distorted and 'flow' more easily than those of a more rigid nature.

Thixotropic, rheopectic, and dilatent behaviour in suspensions influence the viscosity and so affect the flow properties. Thixotropy is particularly troublesome in ceramic slip-casting processes, because if it is appreciable it may hamper the smooth flow of the suspension from the slip-house and give incomplete or poor shapes in the mould.

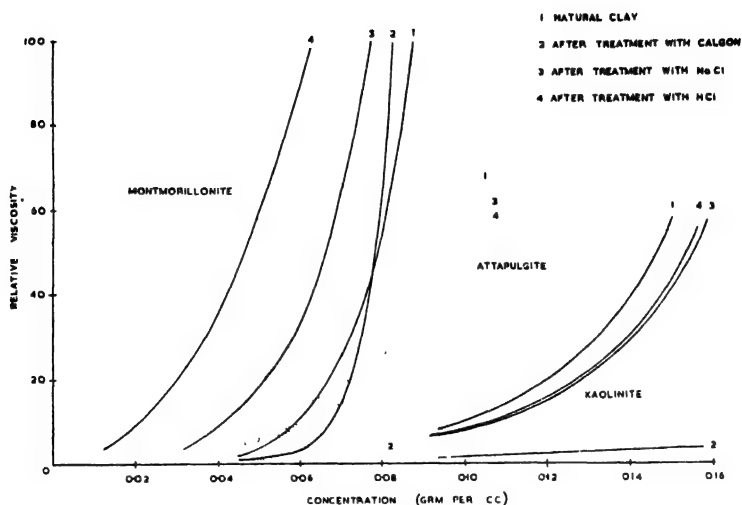


FIG. VIII.23. THE APPARENT VISCOSITY/CONCENTRATION RELATIONSHIP OF KAOLINITE, MONTMORILLONITE AND ATTAPULGITE CLAYS IN THE PRESENCE OF VARIOUS ELECTROLYTES

The **temperature of a suspension** has a small effect in so far as the viscosity of the suspending medium is changed. Other factors are of so much greater importance that the temperature changes normally encountered in practice are of little consequence in ceramic slip practice.

VISCOUS AND PLASTIC FLOW

As the water content of a suspension is reduced relative to the amount of solid matter, the lubricating effect of the liquid medium is lessened. The separation between individual particles becomes so small that free flow is prevented; the resistance to shearing forces increases and when it is sufficiently great and the mass is then deformed, the change in shape is permanent. Unlike true *viscous flow* which is a feature of dilute slips and suspensions, *plastic flow* implies that a certain yield value must be exceeded before any deformation can take place. Viscous flow is reversible, i.e. the distortion produced by an applied force is relieved immediately the force is removed and the body reverts to its former condition. In plastic flow this is not the case—flow does not occur until the distorting force reaches a certain amount and

when the force is removed, a plastic body has a permanent set and does not return to its original shape. There is no sharp dividing line between the two types of flow but a gradual transition as the concentration of solid material in suspension increases.

PLASTIC BODIES

PLASTIC pastes, such as are commonly employed in the clay-working industries, may be regarded as intermediate between solids and viscous liquids. When pressure is applied to a liquid the latter at once commences to flow and continues to do so at a velocity proportional to the pressure. A solid undergoes no appreciable change until its structure is broken down by the pressure. A plastic paste has an intermediate behaviour; on the application of a steadily increasing pressure it appears to be immobile until a critical pressure is applied, after which it behaves like a liquid and—so long as the pressure is maintained—it flows with a velocity proportional to the pressure.

Scott Blair¹ and Bingham² have studied the characteristics of plastic flow by comparing the extrusion volumes of clay pastes through an orifice on the application of a steadily increasing pressure. There are four recognisable stages which are demonstrated in Fig. VIII.24 and explained by Scott Blair as follows.

(a) A region in which no flow takes place although pressure is being applied to the mass.

(b) Above a certain critical yield point, movement or deformation of the mass of clay as a whole occurs. This may be regarded as 'slipping' between the plug of clay paste and the walls of the tube, caused by a water film which may have been forced out of the 'plug' by the applied pressure.

(c) At higher pressures, shearing begins between the layers of clay particles—a region of 'mixed flow' ensues.

(d) Finally, a state is reached where the shearing of clay layers is complete and streamline flow occurs. This is similar to the viscous flow of a true liquid because the shearing ratio varies linearly with applied force, but as Fig. VIII.24 shows, the straight portion cannot be produced back to cut the pressure axis at zero. The point where the downward extension of the streamlined flow region (shown dotted) touches the pressure line is termed the *yield value*, and is regarded by Bingham as a direct measure of the plasticity of the material—a hypothesis which is not accepted by several well-known authorities, although it is a frequently quoted figure to describe the properties of plastic clay masses.

If the rate of flow (v) of a truly viscous liquid is expressed as proportional to the pressure applied (F) the flow of plastic bodies might be similarly represented as a function of $F - f$ where f is the *yield value*.

Thus the Bingham equation for plastic flow is expressed as

$$v = k\mu(F - f)$$

where k is a constant and μ is termed the *coefficient of mobility*. In the limiting case

¹ Scott Blair, G. W., *Trans. Eng. Ceram. Soc.*, 30, 138, 1931.

² Bingham, E. C., *U.S. Bur. Stand. Sci. Paper*, No. 278, Vol. 13, 309, 1916-17.

when $f = 0$ then the expression simplifies to the viscosity relationship for the flow of ideal liquids.

$$u = \mu F \quad (\text{cf. } F = \eta v)$$

Therefore in this case, the coefficient of mobility becomes synonymous with the coefficient of fluidity (φ) or the reciprocal of viscosity.

Scott Blair has suggested that the 'Bingham yield value' should be termed the *static rigidity value* and he considers that the term *yield point* should be reserved for the pressure at which flow just commences. He regards the slope of the pressure/flow line in the region of streamline flow as the *pseudo-viscosity* of the system.

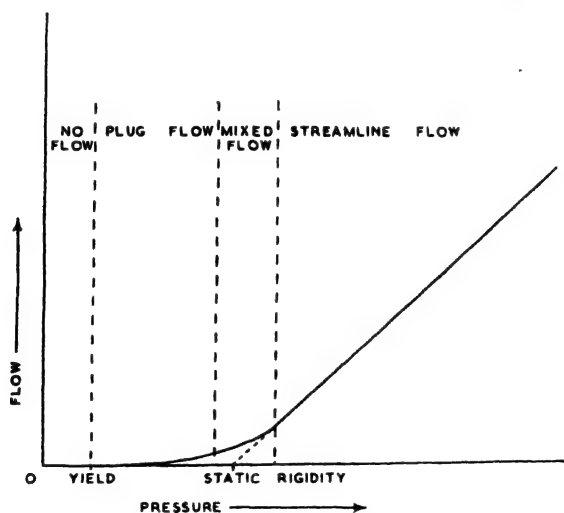


FIG. VIII.24. THE STAGES IN PLASTIC FLOW
(after Scott Blair)

The 'Bingham yield value' or the 'static rigidity' is regarded by some writers as a measure of the coefficient of thixotropy, but, although many clays which exhibit thixotropic behaviour have a high coefficient, this is not the only factor contributing to the absolute value.

The 'Bingham yield value' increases with the concentration of solid particles and is pronouncedly influenced by the presence of electrolytes. Thus, some clays which exhibit a marked degree of plastic behaviour in the natural state, may be converted to a liquid with virtually true viscous behaviour on the addition of a small percentage of electrolyte.

Norton, Johnson and Lawrence¹ have investigated the influence of particle-size on the initial yield point of a hydrogen-ion saturated kaolinite. Their results suggest that an equation of the type

$$\text{Yield point} = kC^n$$

¹ Norton, F. H., Johnson, A. L. and Lawrence, W. G., *Trans. Amer. Ceram. Soc.*, 27, 149, 1944.

adequately describes the behaviour, where C is the concentration of solid particles and n is 3 for all the size-fractions considered. The value of k increases rapidly as the particle size is reduced.

The property of plastic flow is due to the cohesion between the solid and liquid constituents, which together form an apparently uniform mass in which the liquid acts as a lubricant thereby facilitating the movement of the solid particles and simultaneously restraining them from being separated far from each other. The extent of this cohesion depends on the affinity between the particles of solid and liquid; it is great in plastic materials like clay, which have a high capacity for being deformed by pressure without the individual particles being separated from each other, whilst materials in which the cohesion is low do not form good pastes and are termed non-plastic materials.

Care must be taken, however, not to confuse 'plastic flow' with the 'plasticity' of a clay paste. They are related in some senses, but they are not identical.

PLASTICITY

ANY attempts to define the property of *plasticity* must be, by present standards, not fully descriptive. Brongniart in 1844 wrote of plasticity 'on a souvent parlé de cette propriété on semble la connaître, mais on n'en a qu'une vague idée', and this comment is still applicable to the present day.

Plasticity is manifested by some materials which are capable of being deformed or changed in shape when under stress. Such changes are permanent and remain after the deforming force is removed. In this sense, plasticity is not unlike malleability in metals although the force required to change the shape of a plastic body is far less than that required for a malleable one.

Macey¹ considers that, in the widest sense, plasticity embraces *all* the relationships between the stress and resulting strain in a body which exhibits plastic flow.

In an attempt to narrow the scope of definition the term *workability* is sometimes used which defines the ease with which a paste can be spread or otherwise made to change its shape. This is the property which most writers describe, although they refer rather loosely to 'plasticity'.

Many materials are plastic, but clays are unique in the fact that their plasticity is destroyed (though their shape is retained) by removing the water which appears to be essential to their plasticity. Some materials, such as glass are plastic when hot, but rigid when cold; others are plastic only when under great pressure and become rigid when the pressure is released. Others—like rubber—are plastic when cold, but are hardened by heat if they contain sulphur or some 'vulcanising' agent. Clay is unique in the ease with which its plasticity can be developed, combined with the fact that this property is destroyed merely by the removal of the water from the material. Plastic clay differs from most other plastic substances in having a high cohesion when dried and also in having a high binding power; to these it owes its usefulness.

A plastic substance differs from a viscous liquid and from an elastic solid, because both of these regain their original shape when the deforming force is removed. At the same time, the plastic state appears to be intermediate between the

¹ Macey, H. H., *Trans. Brit. Ceram. Soc.*, 43, 5, 1944.

two extremes of solid and liquid, as plastic materials possess some of the properties of both. Thus, a plastic substance, under great pressure, flows like a viscous liquid, but when the pressure is removed it retains its shape like a solid; it has the appearance and general behaviour of a soft and extensible solid, yet when sufficient pressure is applied its fluid properties predominate.

Plastic materials appear to be divisible into two groups:

(a) *Homogeneous substances* which are plastic under certain conditions of temperature, but not under others, e.g. glass, sulphur and many similar materials are plastic when partly melted. This plasticity appears to be analogous to the viscosity of liquids. Although experimental evidence is not available, it is possible that some of these apparently homogeneous substances may consist of solid and fluid phases. Plastic behaviour has also been reported in metals and some crystals, where it is attributed to slipping at crystal defects and along glide planes.

(b) *Multi-phase substances* which owe their plasticity to the simultaneous presence of solid particles and of a fluid which acts as a lubricant and also as a bonding agent for the solid particles.

Plastic ceramic materials, putty (whiting and oil), and many other synthetic plastic materials belong to this group. Such substances consist of solid particles surrounded by films of fluid which form a viscous coating sufficiently thick to permit the particles to move relatively to each other when subjected to a pressure which is less in one direction than in others (i.e. to a shearing force). Highly mobile liquids with a low viscosity cannot be used to produce a plastic substance, as the films are insufficiently buoyant and adherent. Water is satisfactory with clays as it has a moderate viscosity, though under some conditions more viscous fluids will give a greater plasticity; thus, certain oils, some organic solvents, and glycerin may be used and have the advantage, for some purposes, that the plastic product containing them does not 'dry'. Oils are sometimes used instead of water by crucible makers, etc., to produce a very plastic mass, which can be 'dried' with less risk than when water is used. Hexylamine glycol has been tried, with considerable success, as a replacement for water in extruding clays—because the amounts required to form a plastic mass are small, bodies of low density can be produced. The cost of the raw material, however, limits its use to small-scale manufacture.

THE NATURE OF PLASTICITY

It is generally accepted that plasticity is associated mainly with particles which are of colloidal size, therefore it is to be expected that it will be related to the fundamental concepts of the colloidal micelle.

Clay particles when suspended in water are surrounded by a hydrosphere within which are contained ions of different charges. Around the ultimate particle there is a layer of negatively-charged ions and these are balanced by a 'swarm' of cations which are diffused throughout the hydrosphere, which varies in size depending on the number, size, charge, and degree of hydration of the cations (see p. 439). When the hydrosphere is large, the particles in suspensions are at the maximum separation and free, viscous flow is possible as a result of the excess water content. On the other

hand, if the hydrosphere is reduced, the separating water film becomes less and more cohesion results.

The counter-cations provide links between the colloidal particles and rigidity in linkage or 'plasticity' develops. The application of a shearing force causes movement of the charged particles, but an equally stable system is readily formed, which retains its new shape after the removal of the force. Consequently small, unhydrated cations adsorbed around a clay particle give greater plasticity than larger, hydrated ones, all else being equal. Hydrogen clays are thus superior in plasticity to those containing sodium ions.

Plasticity is associated with the formation of water films of a certain order of thickness around each grain. If more than the required amount is present the 'free water' permits flow with a reduction in the plastic properties. At much lower contents of water, the individual particles touch and plasticity is destroyed. Plasticity is thus a function of the water content, the peak value depending on the surface area capable of being wetted. These adsorbed water films appear to have an induced structure by virtue of the surface with which they are in contact, and a continuum is thus formed which surrounds all the particles and introduces a degree of rigidity and at the same time an ease of deformation.

The thickness of the water film which is present in a clay at maximum plasticity is difficult to calculate with certainty but Norton and Hodgdon¹ have deduced that under a pressure of 8 kg. cm.⁻² the film thickness varies slightly with different clays as follows:

Film thickness ($1 \text{ \AA} = 10^{-8} \text{ cm.}$)	
Clay	\AA
China clay	2100
Ball clay	2400
Brick clay	3100
Bentonite	3400

Mattson² has estimated that in soil clay the thickness of the water film is about 700 \AA although this may not have been at maximum plasticity.

It is interesting to record that if water separates two parallel plates the attractive force between them when the separation is 2000 \AA is 8 kg. cm.⁻². For this reason alone the plasticity of particles would be expected to be at a maximum when the water film is of that order of thickness.

Macey³ visualises that water in the immediate vicinity of the surface of clay particles takes on a structure resembling that of ice. The further they are from the surface the less is the influence exerted on the molecules of water, hence the induced structure becomes less rigid. When the separation of the particles is small the rigidly bound water films conjoin, thereby forming a continuum throughout the plastic mass.

Norton,⁴ however, suggests that the only forces between particles in a plastic mass are (a) the repulsive forces between particles and (b) the surface tension of the

¹ Norton, F. H. and Hodgdon, F. B., *J. Amer. Ceram. Soc.*, 15, 191 1932.

² Mattson, S., *Soil Sci.*, 33, 301, 1931.

³ Macey, H. H., *Trans. Brit. Ceram. Soc.*, 41, 73, 1942.

⁴ Norton, F. H., *J. Amer. Ceram. Soc.*, 31, 236, 1948.

water between them which tends to draw them together. At maximum plasticity, the water film fills only the narrow capillaries between the individual particles and so behaves as a *stretched membrane*. At higher water contents the tension is relieved, hence the force holding the particles together is lessened. With less water, the envelope surrounding all the particles will be broken and the plasticity destroyed.

Johnson has pointed out that the 'stretched membrane' theory takes no account of and offers no explanation for the behaviour of added electrolytes, which can reduce a plastic paste to a fluid liquid without any change in the water content.

It is probable that many of the anomalies in the behaviour of plastic masses may be attributable to the fact that two different mechanisms may give rise to plastic behaviour.

A flocculated system will show plasticity at a comparatively low water content. In this condition, the individual clay particles are known to agglomerate and settle to a close-packed system. Dilatency (p. 445) is often a feature and it may be this phenomenon which gives rise to a yield point, beyond which the breakdown of agglomerates coupled with particle orientation permits a streamlined flow. On the other hand, a deflocculated system will also exhibit plasticity, but at a much higher concentration of solid particles. Conditions are such that thixotropy is possible, so that a small applied force causes no yield, but at increased pressure, the structure breaks down and gives rise to streamlined flow.

FACTORS AFFECTING PLASTICITY

CLAYS differ greatly in the amount and quality of their plasticity. The 'fat' or 'strong' clays undergo a large change in shape on the application of a small force; 'lean' or 'short' clays undergo a much smaller change of shape and require a greater force to make the change appreciable; some clays are both 'strong' and 'short', i.e. they require a large force to deform them and change only slightly in shape before being ruptured. Hence, in comparing the plasticities of clays, it is necessary to include the amount of change of shape as well as of the force necessary to produce it.

Omitting, for the present, those materials in which the plasticity is due to the use of oil or of added materials other than water, the plasticity of clays is affected chiefly by:

1. The effect of water on the solid particles and colloidal phenomena connected therewith.
2. The size of the solid particles.
3. The composition of the solid particles.
4. The shape of the solid particles and their internal structure.
5. The aggregation of the solid particles.
6. The surface area of the solid particles and their intermolecular attraction.
7. The presence of other materials which may have an influence on the properties of the particles.
8. The orientation of particles in the mass.
9. The previous history of the material.

Influence of Water-Content. Plasticity is exhibited by clays within a comparatively narrow range of water content. Above a certain value the clay mass becomes

a mud or a slip whilst a dry clay is virtually devoid of plasticity. The maximum plasticity of a clay is developed at a specific water content which corresponds with a film around each particle about 2000 Å thick.

There is a range, however, over which the plasticity is reasonably high, which might be termed the range of workability. In some clays, this may extend over a wide range of moisture content, but, in others, the range is exceedingly small. The principal factor which influences the workability range is the amount of colloidal or fine-grained material. The greater is the effective surface area of solid the larger is the volume of water required to form a continuous film. Furthermore, more water is required to cause a specific increase in film thickness when the surface area of the particles is large.

The proportion of water required to produce the maximum plasticity in any clay varies according to the extent to which the clay can be made plastic. Thus, a dry clay, which is potentially highly plastic, such as a ball clay, usually requires much more water to develop its plasticity to the fullest extent than a clay, the total potential plasticity of which is low. Table VIII.IV gives some figures which are applicable to various clays, but no closely concordant figures can be obtained, as clays vary so greatly.

TABLE VIII—IV. WATER REQUIRED TO DEVELOP
MAXIMUM PLASTICITY

<i>Material</i>	<i>Percentage of water required</i>	<i>Material</i>	<i>Percentage of water required</i>
Brick clays	15–25	Flint clays	15–24
Fireclays	15–35	China clays and kaolins	18–50
Shales	15–25	Ball clays	25–50
Pottery clays	15–50		

For some purposes it is better to express the proportion of water volumetrically instead of by weight.

The relative volumes of water and solid matter in a moist mass of clay may be represented by the symbol ϵ .

The ratio $\epsilon = \frac{\text{volume of water}}{\text{volume of solid}}$ in a plastic clay is invaluable to constructional and waterworks engineers who have to deal with the effect of pressure on wet clay. It is most conveniently determined by (i) weighing the clay in air (W_1); (ii) weighing it when suspended in paraffin (W_2); and (iii) weighing after drying at 110° C. (W_3).

If the specific gravity of the paraffin is S :

$$\epsilon = \frac{S(W_1 - W_3)}{(W_1 - W_2) - (W_1 - W_3)S}$$

When ϵ is less than 0.35, flow cannot take place without rupture of the particles. Many surface clays with $\epsilon = 0.75$ have a safe load carrying capacity of 1 ton per sq. ft. so long as there is no evaporation. When $\epsilon = 2.70$ the weight of water and solid

matter are equal and the mass is 'sticky' and useless for ceramic purposes; its bearing power is nil and it is practically a viscous fluid.

According to Berridge, when a plastic clay is at its maximum density, $\epsilon = 0.46$, but this figure must vary with different clays.

The amount of water required to make a suitable paste is dependent to a large extent on the nature of the particles constituting the mass. Thus, coarse particles will require less water than fine-grained clays and the maximum plasticity is developed in an 'aged' paste with less water than is required for a freshly-made one, because in the 'aged' paste the water is more uniformly distributed.

The presence of soluble salts and organic matter in either the clay or the water also influences the amount of water required to develop the maximum plasticity.

The proportion of water required to develop the most suitable plasticity also depends on the pressure used in shaping or testing the plastic paste. Thus, a paste for hand-moulded bricks must be softer and usually more plastic than that used for machine-pressed bricks. J. W. Mellor¹ found that with different pressures the maximum plasticity of a certain clay occurred with the following proportions of water:

TABLE VIII—V. EFFECT OF PRESSURE ON PLASTICITY

<i>Pressure kg. per sq. cm.</i>	<i>Water per cent</i>	<i>Pressure kg. per sq. cm.</i>	<i>Water per cent</i>
200	5.6	50	19.2
150	8.8	25	23.0
100	12.5	1	26.5

This Table shows that less water is needed to produce a suitable paste for use in presses; failure to realise this has caused many defective articles to be produced.

Effect of Size of the Particles. Various investigators have attributed plasticity to the extreme smallness of the grains of a material, because various materials, usually considered to be 'non-plastic', may, when very finely ground with water, develop a small amount of plasticity. Quartz and limestone, when ground to pass a 200-mesh sieve and then mixed with a small proportion of water, have, according to Wheeler, a slight plasticity, but do not hold together on drying. Orton found a similar effect with ground glass, and Cohn and Atterberg found that precipitated barium sulphate and calcium fluoride are plastic when wetted. Wet-ground felspar, which has been allowed to stand for some time, has, according to Daubree, a slight plasticity.

The plasticity developed by grinding non-plastic materials is, in all cases, so small that, whilst it must be admitted that the size of the particles certainly is in some way connected with plasticity, it is only one of the factors involved. That it ought not to be overlooked is shown by the fact that, if the fine particles of a plastic clay are all removed, the residue usually loses its plasticity. On the other hand, clays composed of the finest grains are not necessarily the most plastic and some clays consisting almost wholly of fine grains are not highly plastic. It is certain, however, that the size of the grains has some effect, as the plasticity of a clay may often be

¹ Mellor, J. W., *Trans. Eng. Ceram. Soc.*, 21, 25, 1922.

increased by finer grinding, whilst the inclusion of coarser grains decreases the plasticity. At the same time, plasticity is not wholly due to the small size of the particles, because when a clay is decomposed by heat into silica and alumina the resulting particles should be smaller than the original grains, and, consequently, should be more plastic when wetted; yet this is not the case, as such particles are entirely non-plastic.

Clay particles also differ from non-plastic materials which have been very finely ground inasmuch as the latter, when dried, have a very low cohesion and form a very friable mass; clay particles, on the contrary, form a strong mass when dried. **Effect of Composition of the Particles.** It is sometimes stated that, as plasticity is largely a mechanical property, it must be independent of the composition of the clay. This is incorrect, for though there is no simple relationship between the major constituents of a clay and its plasticity, there appears to be a fairly definite connection between the amount of colloidal matter and the plasticity, though this is difficult to prove.

The influence of mineral type on plasticity has not been established for several reasons. In order to be able to compare the properties of two mineral entities not only have particles of similar size to be prepared, but the shape of such particles has to be identical. In plasticity measurements where so many other characteristics exert an influence the elimination of all variables other than mineral type is well nigh impossible.

Currie¹ has attempted to compare the plasticity of various kaolin minerals in fractions where the surface area is kept constant. In these cases although the different minerals showed variations in behaviour, all other factors being constant, the order of the differences was slight compared with the influence of grain-size, shape or electrolyte content. It is not unlikely that although some substances when added to others are known to increase the plasticity, it may be more the result of the increase in the fineness of grain rather than the nature of the mineral itself.

Bentonites are commonly added to non-plastic bodies to increase their plasticity. Although, undoubtedly, such clays increase both the green and dry strengths of bodies to which they are added, materials which include them have a short working range before fracture. The so-called *livesite*, *illite* or *sericite* clays are better in this respect because they deform readily and can withstand considerable distortion before rupturing; they do not impart such great strengths as do the bentonite clays.

The type of cations associated with a clay has a pronounced influence on the plasticity. This aspect is considered more fully in the section on the *influence of electrolytes*, but, in the broadest sense, the exchangeable cations are part of the composition of a clay and, as such, affect the plasticity.

Various organic colloids, including tannin, lignin, and humus may be present in a clay and affect the plasticity. Their mode of action is to form *protective colloids* around the clay particles and to enhance the colloidal properties. Many ball clays owe their high plastic properties to associated lignin, but other clays, which contain no organic matter are equally plastic.

The Effect of the Shape and Structure of the Particles. The plasticity of clays is frequently attributed to their lamellar or platey nature. This is supported by the fact

¹ Currie, T. E., Leeds University B.Sc. thesis, 1951.

that some minerals with a characteristic fibrous or platey nature, e.g. glauconite, mica, pyrophyllite and talc, develop plasticity when they are finely ground, whereas other minerals which have a more regular crystal habit, e.g. cubic and rhombohedral, are not nearly so plastic, even when crushed to about the same particle-size.

Whilst a lamellar nature in particles is useful in producing plasticity it is not the only suitable shape. Fibrous crystallites, such as those found in attapulgite, and halloysite, are if anything, capable of producing more plastic masses.

Undoubtedly, the surface area per unit weight of particles is a contributing factor to the plasticity and for this reason fibrous and platey particles would be superior to those of spherical or cubic shape, but the orientation or packing of the crystallites is probably of equal or greater importance.

Effect of Aggregation of the Particles. Evidence is accumulating which seems to show that the structure of the ultimate particles and their aggregation into larger ones has an important influence on plasticity, and it has even been suggested that plastic clays are composed of 'crumbs' each consisting of a felted mass of lath-shaped or needle-shaped crystals. On the other hand, Aleksieff and Cremiatschensky have found that very fine-grained and very coarse-grained clays are both less plastic than those containing both large and small grains, and Mellor¹ has suggested that a distribution of grains of various sizes which permits the closest possible packing gives a maximum plasticity, whilst Schurecht² concluded that:

- (a) Loosely cemented aggregates of clay grains are more plastic than closely compacted ones.
- (b) Fine-grained aggregates are more plastic than coarse-grained ones.
- (c) Flocculated aggregates are more plastic than deflocculated ones.
- (d) Flocculated aggregates are more plastic than cemented ones.

He states that the reason some clays retain their plasticity after removing the fine portion, whilst others lose it, is due to the former consisting of loosely aggregated bundles of clay grains which can be broken down fairly easily by stirring, yielding a fresh supply of fine grains, whilst the cemented particles require a much greater force for their disruption. According to him, more of the finest particles can be produced in ball clays than in kaolins, because the flocculated aggregates in the former are composed of smaller grains than in the latter, and for this reason a greater plasticity can be developed. Schurecht also found that the addition of an alkali to a clay-suspension increased the strength of ball clays in the dry state to a greater extent than that of kaolins; he attributed this difference to the smaller particles composing the aggregate 'crumbs' in ball clays.

The fact must not be ignored that the larger particles of clay are simply agglomerations of the smaller particles and possess the same properties, though some aggregates break down more readily than others.

Effect of Surface Area and Intermolecular Attraction. On account of their fineness, grains of plastic clay have a large surface area, and, consequently, exhibit surface phenomena (including intermolecular attraction and colloidal properties) to a very marked degree. It is not unreasonable therefore to conclude that the surface

¹ Mellor, J. W., *Trans. Eng. Ceram. Soc.*, 21, 91, 1921.

² Schurecht, H. G., *Bull. Amer. Ceram. Soc.*, 153, 1923.

area of the particles present in a plastic mass contributes in no small measure to the ultimate plasticity.

In a mass of particles two factors contribute to the total surface area, viz. the fineness of grain-size and the particle shape.

1. The influence of grain-size may be demonstrated by considering fixed weights of spheres of two different sizes, having radii of $10R$ cm. and R cm. Their volumes are:

$$\frac{4}{3}\pi(10R)^3 \text{ c.c. and } \frac{4}{3}\pi R^3 \text{ c.c., respectively.}$$

If the specific gravity of the material composing the spheres is ρ , the weight of each sphere is simply its volume multiplied by ρ .

The number of spheres in 1 gm. will therefore be

$$\frac{1}{\text{weight of each sphere}} \quad \text{i.e.} \quad \frac{1}{\frac{4}{3}\pi(10R)^3\rho} \quad \text{and} \quad \frac{1}{\frac{4}{3}\pi R^3\rho}$$

in the two cases.

As the surface area of a sphere is equal to $4\pi(\text{radius})^2$, the total surface area in 1 gm. of spheres of $10R$ and R cm. radius will be

$$\frac{1}{\frac{4}{3}\pi(10R)^3\rho} \cdot 4\pi(10R)^2 \text{ sq. cm. and } \frac{1}{\frac{4}{3}\pi R^3\rho} \cdot 4\pi R^2 \text{ sq. cm.}$$

respectively, i.e.

$$\frac{3}{10R} \quad \text{and} \quad \frac{3}{R}$$

Thus the result of decreasing the size of particles by 10 times increases the *specific surface area* by the same factor.

2. The influence of particle shape on the surface area may be assessed on a sphere, cube, plate and needle or fibre of comparable sizes. In Fig. VIII.25, the long dimension in all cases (diameter in the case of the sphere) is $2R$ cm., and the short dimension is XR where X is considerably less than unity. The density of the material in all cases is ρ .

In a case where the plates and fibres have a thickness to size ratio of $1:10$, $R = 1$ and $X = 0.1$, so that the specific surface area, i.e. surface area per gm. of the four shapes of comparable sizes is in the following ratio:


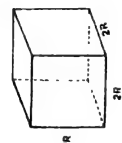
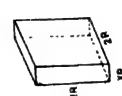

$$\text{Sphere : cube : plate : fibre} :: 3 : 3 : 22 : 41$$

For this reason, platey and fibrous particles exhibit greater plasticity than do spherical or cubical ones.

The values derived from the data in Fig. VIII.25 are for ideal crystals, but the ultimate crystallites in clays and other ceramic materials are often far from being so perfect. Transported particles, either through the medium of air, water or glaciers, are invariably roughened and fractured and the specific surface area may be very much greater than would be predicted from particle-size measurement. R. H. S. Robertson suggests that the term *roughosity* be used to describe the deviation of the surface area of a particle from the ideal.

The Effect of Electrolyte and Flocculants. The addition of soluble salts to clays may influence the plasticity considerably. Not only may the repulsive force between

FIG. VIII.25. VARIATION OF SURFACE AREA WITH DIFFERENT PARTICLE SHAPES

	Sphere	Cube	Plate	Fibre
				
Volume of one particle	$\frac{4}{3}\pi R^3$	$8R^3$	$2R \times 2R \times XR = 4XR^3$	$2R \times XR \times XR = 2X^2R^2$
No. of particles per gm.	$\frac{1}{\frac{4}{3}\pi R^3 \rho}$	$\frac{1}{8R^3 \rho}$	$\frac{1}{4XR^3 \rho}$	$\frac{1}{2X^2R^2 \rho}$
Surface area of one particle	$4\pi R^2$	$6 \times (2R \times 2R) = 24R^2$	$2(2R)^2 + 4(2R \times XR) = 8R^2 + 8XR^2$	$4(2R \times XR) + 2(XR)^2 = 8XR^2 + 2X^2R^2$
Surface area per gm.	$\frac{4\pi R^2}{\frac{4}{3}\pi R^3 \rho} = \frac{3}{R \rho}$	$\frac{24R^2}{8R^3 \rho} = \frac{3}{R \rho}$	$\frac{8R^2(1 + X)}{4XR^3 \rho} = \frac{2(1 + X)}{XR \rho}$	$\frac{2XR^2(4 + X)}{2X^2R^2 \rho} = \frac{4 + X}{XR \rho}$

particles in the mass be altered as a result of cationic or anionic absorption but the surface tension of the liquid medium may be changed. Both effects have a pronounced influence on the plasticity of the clay mass. As an example of the former the action of alkalies and acids may be cited. When only 6 lb. of a mixture of sodium carbonate and sodium silicate is added to a ton of some kinds of clay, it can be made into a liquid with less than 20 per cent of its weight of water. If just sufficient acid is added to neutralise the 6 lb. of alkali, the whole mass becomes solid immediately.

The effect of minute proportions of acids, alkalies and various electrolytes on the plasticity of clays has been the subject of innumerable experiments but the theoretical aspects of the effects of absorbed cations on plastic clay bodies is not fully understood. It may be that the bonded water in intimate contact with the clay surface is influenced by the associated cations.¹ The work of Speil² and Sullivan and Graham³ suggests that the greater the cationic concentration near the surface of the colloidal particle the more strongly will water be held. Small cations of high valency (e.g. Ca^{2+} , H^+ , etc.) when absorbed will tend to give a higher proportion of bonded water than those of large size and small charge. In a plastic mass where the particles are very close, the absorbed water films around each colloidal grain merge together, so the force required to rupture such masses will depend on the degree of bonding of the water. The plasticity in terms of yield point and breaking strength in torsion are close to the theoretical predictions of the Hofmeister series as shown in Fig. VIII.26. Because the water films surrounding clay particles are more flexible when alkali cations are absorbed, such clays are capable of greater deformation although they rupture more readily than do hydrogen or calcium clays.

More water is required to produce a plastic mass of a particular strength with a hydrogen and calcium clay than with one containing sodium as the exchangeable cation; so for a particular water content, hydrogen and calcium clays require a greater moulding pressure, but the green body is stronger and less liable to loss of shape than sodium clays.

In general, the range of water content over which the clay is workable is greater with a sodium than with a hydrogen or calcium clay although this is affected by other factors also.

The addition of a material which reduces the surface tension of water also liquefies a plastic mass. Such agents, which permit more concentrated suspensions to be used as casting slips, yet without introducing salts deleterious to refractory properties, are finding increasing use in industrial applications.

The Effect of the Presence or Addition of Other Materials. The plasticity of clays can often be increased or decreased by the addition of other substances than those mentioned above, but the mode of action of many of these is far from clearly understood.

It is not difficult to appreciate that the addition of colloids increases plasticity, although artificial mixtures are seldom as plastic as a natural clay of the same composition. The addition of a *non-plastic*—such as quartz or fired clay (grog)—reduces the plastic behaviour.

¹ Mattson, S., *Soil Sci.*, 33, 301, 1932.

² Speil, S., *J. Amer. Ceram. Soc.*, 23, 33, 1940.

³ Sullivan, J. D. and Graham, R. P., *J. Amer. Ceram. Soc.*, 23, 39, 1940.

Air incorporated in a clay-paste has an adverse effect on its plasticity, so that such a clay appears to be short, but recovers its plasticity when the air has been removed by 'wedging', 'rolling', or by de-airing under low pressure. Incorporated air may also cause blisters in the goods and is a common cause of laminations and warping. Much of the air in plastic pastes is introduced mechanically during preparation; most of it may be removed by attaching an air-pump to a pugmill in a suitable manner and passing the clay paste through the mill.

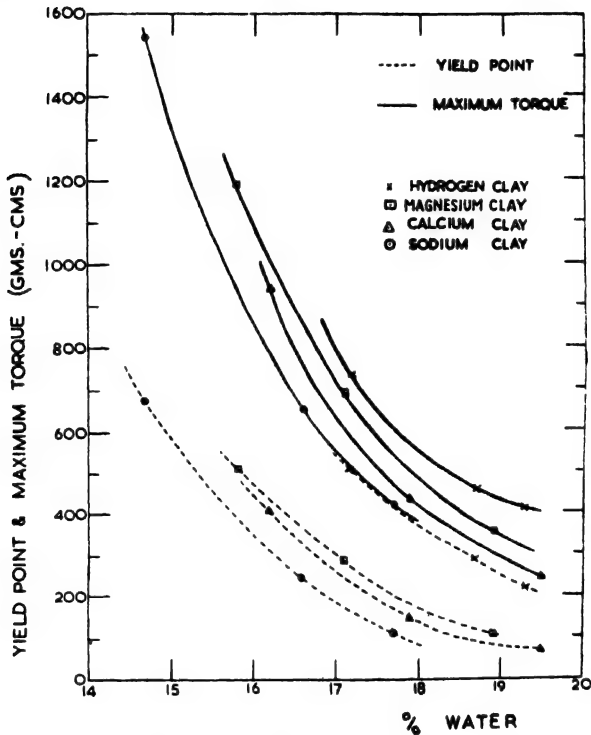


FIG. VIII.26. THE EFFECT OF DIFFERENT ADSORBED CATIONS ON THE YIELD POINT AND THE MAXIMUM TORQUE OF CLAY MASSES AT VARIOUS WATER CONTENTS

The amount of air worked into clay during the preparation of a paste or body is much larger than is generally realised, and its adverse influence is often very serious. Lovejoy and Covan¹ have found that removing the air from the clay as it enters an extrusion (wire-cut) machine lessens troubles in shaping and increases transverse strength and shrinkage.

The proportion of air in a plastic clay may be ascertained by placing a weighed quantity of the clay in a vessel of water, the clay being placed beneath a large inverted glass funnel and burette, previously filled with water by suction. On heating the

¹ Lovejoy, E., and Covan, H. E., *J. Amer. Ceram. Soc.*, 14, 533, 1931.

water to boiling, the clay disintegrates and the air is released in the form of small bubbles which rise into the burette and can there be measured. A more accurate eudiometer may be used if required, but for routine tests is not necessary.

The Effect of the Orientation of Particles in the Mass. The plasticity of clay masses is undoubtedly influenced by the alignment of the particles of the predominant minerals particularly those which are plate-like. This may be demonstrated very readily with an oriented mass prepared by settling an air-free clay suspension and removing excess water by decantation or suction, followed by careful drying under vacuum. The mineral plates in such a mass will be arranged so that their basal section is at right angles to the settling direction.

If a force is applied to such a plastic mass at right angles to the oriented plates (i.e. downwards) the mass has a high yield value. Should the force be applied along the direction of 'bedding' (i.e. horizontally) flow commences at much lower applied pressures, because the plates slide on each other. A randomly-oriented mass will normally be intermediate in behaviour. Macey¹ has shown that if a plastic clay mass is continuously subjected to alternating tensional and compressive stresses, a looseness of structure develops and eventually small stresses produce large deformations. This phenomenon is attributed to the gradual orientation of mineral flakes and has been termed *back-lash*. When the clay contains few small particles, the mass exhibits *shear hardening*. The application of alternating forces causes orientation which permits slipping in a direction parallel to the mineral plates; after some time, however, dilatent conditions are set up and a hardening of the structure takes place. This has an important bearing on the shaping of clay by extrusion processes, e.g. wire-cut bricks and salt-glazed pipes.

Effect of Previous History. The treatment (either natural or artificial) which a clay has undergone has a large effect on its plasticity. The primary clays are only feebly plastic because they have not been subjected to conditions which would develop plasticity. Many secondary clays, on the contrary, are highly plastic in a natural state but the degree to which they have been compressed has an important bearing. When a clay is air-dried it loses its plasticity, but this is readily restored when the clay is mixed with a suitable proportion of water. If a clay is dried by artificial heat, or, sometimes if it is exposed to tropical conditions, its plasticity after mixing with water is low because of a partial decomposition of the clay or a partial conversion of the colloidal matter into an inert material. For the same reason, clays which have been heated for a long time at any temperature above 500° C. lose their plasticity permanently. Any treatment which alters the colloidal matter affects its plasticity. All these changes are commonly summarised in the statement that the previous history of a clay has an important influence on its plasticity.

POTENTIAL AND ACTUAL PLASTICITY

In considering the plasticity of clays it is necessary to distinguish the *actual* (or *active*) from the *potential* (*kinetic* or *dormant*) plasticity. A dry clay is non-plastic, but on being mixed with a suitable quantity of water it will become plastic, the amount of plasticity depending on the previous history of the clay.

¹ Macey, H. H., *Trans. Brit. Ceram. Soc.*, 47, 259, 1948.

The **potential plasticity** of a clay is an inherent property and is the maximum plasticity which can be developed by suitable treatment of the clay. The **actual plasticity**, on the contrary, is the plasticity at the moment of inspection; it is reduced by drying and may be increased (if this is possible) by mixing the clay with water, by removing some of the non-plastic material (sand, etc.) present, and also by grinding the clay or by subjecting it to any treatment which will increase the proportion of suitable colloidal matter.

To increase the plasticity of a clay until it equals the maximum potential plasticity is extremely difficult and apparently requires a far longer time than is practicable when artificial means are employed.

The term *maximum plasticity* of a clay or clay mixture is used to indicate the greatest plasticity which can be developed by methods in general use, such as fine grinding, thorough mixing, and the incorporation of a suitable proportion of water. This term is not used to indicate the plasticity which might be developed by extraordinary means, such as the prolonged heating of a few grains of material with steam under enormous pressure. When all the maximum plasticity has been developed, the material is usually less plastic than if the potential plasticity could have been made fully available.

A clay or clayey mixture is usually regarded as having attained its maximum plasticity when a portion of it, after being squeezed in the hand, retains an impression of all the fine lines of the skin, yet leaves no appreciable quantity of clay adhering to the fingers. If a clay in this state is mixed with a little more water, it becomes sticky and adhesive, and if still more water is added progressively the clay eventually becomes obviously fluid and devoid of plasticity. A dry piece of clay is also devoid of plasticity; it is too rigid to be deformed by squeezing in the hand and if subjected to a greater pressure it cracks and may fall to pieces. Between these extremes of rigidity (of dry clay) and fluidity (of a clay slip) are innumerable graduations of plasticity and stickiness, depending on the nature of the clay and on the proportion of water added to it.

It also follows that each clay or mixture has an individual maximum potential plasticity depending on the nature of the clay. Thus a china clay cannot, by the artificial addition of more water, or other substances, develop the same maximum plasticity as a first-class ball clay. The actual plasticity of a sample of each clay may be the same if, for example, that of the china clay has been fully developed, whilst the ball clay is in a semi-dry state and of low actual plasticity because it does not contain a sufficient proportion of water.

When more water is added to a clay than is needed to develop the maximum plasticity, the mass becomes sticky or adhesive.

In the clay-working industries it is important to develop the plasticity to a suitable extent, this being part of the 'preparation' of the clay for use.

Increase and Reduction of Plasticity. Many natural clays are potentially, rather than actually, plastic; their plasticity may, therefore, be increased, up to a limit, by mixing them with a suitable proportion of water or in other ways. Some clays, on the contrary, are too plastic or too sticky to be used in their natural state, and must, therefore, be treated in some way to reduce their plasticity.

Increasing Plasticity. The investigation of methods of increasing the plasticity

of clays and ceramic materials is beset with many difficulties; among others is the difficulty of distinguishing between the actual plasticity of a mass and the potential plasticity which may be developed by various means.

The plasticity of a ceramic material may be increased:

- (a) By the addition or removal of a suitable proportion of water.
- (b) By the more thorough incorporation of the water and plastic materials present.
- (c) By the removal of some of the non-plastic material present (usually by converting the material into a slip, allowing some of the non-plastic matter to 'settle out' and then removing the excess of water from the decanted slip).
- (d) By the addition of a flocculating agent to a slip. This may be achieved in several ways such as:
 - (i) Using a substance which on fermentation or other decomposition, produces a free acid, e.g. peat, cellulose extract, etc. The decomposition of carbonaceous constituents contributes to the increase in plasticity of some clays when they are weathered.
 - (ii) Adding a weak acid such as humic, tannic or acetic acid.
 - (iii) Incorporating other flocculating or coagulating agents (see p. 478.)
- (e) By the addition of a substance of a colloidal nature. This would include other clays or gels or a substance which could be converted into a *gel* by subsequent treatment with an acid or on prolonged storage (e.g. colloidal silica, alumina, soluble iron salts and a variety of organic complexes).
- (f) By an electrical treatment which will reverse the electrical charge on the material.
- (g) By grinding and pugging with or without water, which thereby reduces the particle size and increases the amount of hydrolysis.
- (h) By developing thixotropic conditions in the clay body.
- (i) By drying and grinding the clay and using oil instead of water. This is sometimes done when making crucibles and small articles which are shaped by mechanical pressure.
- (j) By removing air from the clay paste by vacuum treatment. Such a process, in addition to developing increased plasticity also results in a better textured body.
- (k) By the process known as *ageing* or *souring*. This is a change which takes place in clay pastes and is dependent to some extent on their colloidal nature. When a clay paste is kept moist and cool for a sufficiently long time, its actual plasticity is increased, the water in it is more uniformly distributed, and the homogeneity and working properties of the clay are greatly improved. Hence, where financial considerations permit, clay pastes are greatly improved if they are allowed to 'sour'. In order that the souring may be effective, an ample quantity of water must be present, and to ensure this, and to prevent surface drying, the clay is usually covered with wet cloths during the souring period, the cloths being renewed or rewetted at frequent intervals. Sometimes the clay is placed in pits or in sumps and covered with water for the required period. The surplus water is afterwards run off and the paste is dug out. Wedgwood and some other famous pottery manufacturers have aged the moist clay by keeping it stored in air-tight boxes for several years.

The effect of ageing or souring is probably chiefly due to the decomposition of the organic matter present, with the formation of dilute acids which coagulate the fine grains of clay and thus increase the plasticity. A similar effect may sometimes be obtained by adding acid direct to a fresh clay; but the results are not quite the same, as when decomposition occurs *in situ* the acid is more uniformly distributed, whereas when added artificially it must be allowed a considerable time before it is thoroughly distributed through the mass.

The presence of an excess of free alkali in clays limits or may even prevent their improvement by souring. Any such excess should be neutralised by the addition of a suitable acid before any increase in the plasticity of the clay can occur. Seger suggested the addition of a suitable proportion of acetic acid to clays before souring, whilst the addition of old vinegar and of wine was, at one time, a common practice amongst some pottery manufacturers.

It has been suggested that the effect of bacteria or moulds present in a clay has an important effect in the souring,¹ but the extent of their influence is not definitely known. In order to increase the proportion of fermented matter some manufacturers have added sugar or honey to their pottery mixtures before souring.

The effect of heat on the souring process is difficult to determine on account of the complexity of the reactions which occur. Rohland has stipulated that the souring should take place in a cool atmosphere, as it is fundamentally a colloidal phenomenon, yet clay slips which are dried by heat are more plastic when re-wetted than those which have had the surplus water removed in a filter press; and H. Spurrier² has found that when souring or ageing clay a temperature of 80–90° C. is preferable to one below 60° F., as the plasticity is increased to a greater extent; A. S. Watts³ has also found that the best conditions for ageing clay are a temperature of 80° F. and relative humidity of 90 per cent.

The increase in plasticity of many clays on ageing is undoubtedly a purely physical phenomenon in which many factors may play a part; a more uniform distribution of water takes place and orientation of particles develops. If a clay paste is allowed to stand the charge distribution on the particles becomes more evenly distributed with a consequent increase in plasticity.

Plasticity may be reduced by the converse of the methods used to increase it. One of the most efficient methods is to heat the clays to about 200° C. Suitable heat treatment can be employed to reduce plasticity to any desired value and it can virtually be completely destroyed by heat treatment at about 500° C.

Pseudo-Plasticity. A modified form of plasticity may be developed in some non-plastic materials by the addition of a suitable viscous fluid, such as oil, or, preferably, an aqueous solution of a gelatinous or gummy material, such as hot starch, dextrin, rubber, sumach, inulin, caramel, gelatin, gum, glycogen, various ferments and enzymes and other colloidal materials.

Such an addition increases the plasticity of the material but does not produce the same result as plastic clay in the fired material, because such organic additions are burned out in the firing. For this reason, such substances are said to produce a

¹ Komuro-Hideo, *J. Kyoto Women's Univ.*, 1, 1, 1952.

² Spurrier, H., *J. Amer. Ceram. Soc.*, 4, 113, 1921.

³ Watts, A. S., *New Jersey Ceramist*, 1, 93, 1921.

pseudo-plasticity which must be carefully discriminated from that of a natural plastic clay. It is important when using such materials to increase the plasticity of a substance, to use a suitable proportion of each. An excess will usually produce 'stickiness' (p. 487) rather than plasticity.

Oiliness is sometimes regarded as a form of pseudo-plasticity, though it is really distinct from true plasticity and from stickiness. It is often due to the presence of oils or oleaginous substances, and, where necessary, may usually be removed by extracting these materials with benzene or other suitable solvent. The oleaginous nature of some clays is destroyed when they are boiled with a solution of alkali which forms a soap; the latter increases the pseudo-plasticity (p. 427) of the clay. The 'oiliness' of some clays is more readily observed when an attempt is made to mix them with water.

MEASUREMENT OF PLASTICITY

As there is no generally accepted definition of plasticity, no one method of measurement can be fully descriptive. The measurement of the change in shape of a mass of a certain size when subjected to a definite force is insufficient, as also is the rate of such change.

Atterberg¹ has summarised some of the various factors which have been proposed as a basis for the measurement of plasticity, viz.:

- (a) The upper limit of fluidity, at which the clay flows almost like water.
- (b) The lower limit of fluidity, at which two portions of the material will not flow together and unite when jerked and shaken.
- (c) The adhesion limit, at which clay ceases to stick to other objects, such as the hands when the clay is squeezed.
- (d) The 'rolling-out limit', at which the clay ceases to be capable of being rolled out into thin cylinders or threads.
- (e) The 'cohesion limit' at which the grains cease to stick to one another.

Atterberg has stated that the range of suitable consistency for working lies between (c) and (d). He found that the moisture content of the flow-limit and rolling-out limit coincides in non-plastic loams but, as the plasticity of a clay increases, these two limits become more and more separated and so constitute the working range of plasticity. He also found that the adhesion-limit is raised by an increase in the proportion of organic matter, but the total plasticity is reduced. Thus, in clays and loams containing much humus, the adhesion-limit is considerably higher than the flow-limit. Where humus is present in only small quantities, or is absent, the adhesion-limit is lower and in most plastic clays it lies below the flow-limit and, consequently, in such materials the range of plasticity is between the rolling-out limit and the adhesion-limit as previously stated. The addition of sand to clay lowers the total plasticity by reducing the range of plasticity, though the adhesion-limit is raised relatively to the others.

Atterberg Number. From a consideration of the foregoing, Atterberg suggested that the plasticity of a clay mixture may be expressed numerically by deducting the percentage of water corresponding to the rolling-out limit from the percentage of

¹ Atterberg, A., *Inst. Mitt. Bodens*, 1, 10, 1911 and 2, 149, 1912.

water corresponding to the flow-limit. Thus, if 40 per cent of water is required to cause the material to flow and 20 per cent is necessary to enable it to be rolled out into cylinders, its plasticity number (*Atterberg Number*) is $40 - 20 = 20$.

He proposed to group clays into four classes:

	<i>Atterberg Number</i>
Class I	17-27
Class II	5-15
Class III	4-7
Class IV	0-1

This method attributes to some substances, such as barium sulphate, a high plasticity, though they are not generally considered to be highly plastic. Atterberg's numbers also correspond very closely to the binding power of clays (p. 488), rather than to their true plasticity, and, as R. Rieke¹ has pointed out, the Atterberg's ranges are not always reliable, the plasticity being also due to properties other than those he has considered. The Atterberg number does not fully describe plasticity but defines only the range of water content over which the property exists.

Rieke, with Seger and others, considers the firmness of the dried material to be a necessary property of truly plastic materials, but this is not correct, as the properties of the dry clay are no guide to the plasticity of the clay paste; the mistake has arisen through confusing 'binding power' with plasticity. A clay to be of value industrially must usually possess both these properties and, in addition to being plastic and easily moulded when in the form of a paste, it must form a strong and compact mass when dried and burned. Such a complexity of properties is not required in other plastic materials.

Several other methods which have been used for the purpose do not measure the plasticity. Thus, it is impossible to use any of the properties of dried clay to indicate the plasticity of clay pastes, though it is an interesting coincidence that the tensile strength of a dry clay is often proportional to the plasticity of the paste. The plasticity can be measured only by means of some property possessed by the plastic paste.

It is equally unsatisfactory to measure the 'binding power' of a clay or clay mixture and to regard that as an indication of the plasticity, because there is no necessary connection between binding power and plasticity. It is also not correct to regard the proportion of colloidal matter present as a true measure of plasticity.

If plasticity may rightly be defined in terms of deformability (p. 755), it is clear that the only rational methods of measuring plasticity must be of a mechanical nature, and that they must measure the pressure required to alter the shape of the plastic mass to a definite extent—possibly at a definite rate or within a definite period of time. Other methods which do not involve these three factors of force applied, change of shape and duration of force, may be convenient for various purposes, but they do not provide true measures of plasticity.

Whichever of the available methods is used, care must be taken to distinguish (a) the potential plasticity, i.e. the plasticity which the material possesses after such

¹ Rieke, R., *Sprechsaal*, 44, 597, 1911.

treatment as will develop the maximum plasticity, apart from the addition of any substance other than water, and (b) the actual plasticity of the material when no water or other material is added. Thus, a dried clay may have no actual plasticity, but a very high potential one.

Many methods have been proposed for the measurement of so-called plasticity. They can be divided into two groups; those in the first determine a property which is indirectly related to plasticity, and those in the second include attempts at a more direct approach.

Indirect methods include measurements of:

(a) The *proportion of water required to develop a paste* of recognisable consistency, as suggested by Atterberg (p. 480) and others. In addition to being indirect, Atterberg's method leaves a large margin for the personal element and is, therefore, undesirable, though it is convenient and has been largely used for comparative tests. It is based on the idea that the plasticity of a material is proportional to the amount of water present, but as it is not the water alone, but the nature of the viscous fluid (of which the water is only one constituent), and the nature of the solid particles as well, which determine the plasticity of a mass, Atterberg's method is fundamentally unsound, but it is a simple and convenient determination for some purposes, e.g. assessing the properties of soils.

(b) The *proportion of colloidal material present*. These methods assume that plasticity is dependent only on the amount of colloidal material present and ignore all other variables.

(c) The *viscosity* of the mass.

(d) The *penetrability* of a 'needle' or steel sphere; these indicate only the softness of the clay mass.

Direct methods of measuring the plasticity of a material are necessarily of a mechanical nature; they involve three variables—force, shape, and time.

(a) *Subjective Methods*. One of the earliest of these methods, which, in spite of its crudity, is still largely used and is very convenient, consists in pressing a small piece of the material in the hand. A paste of a satisfactory consistency for moulding should not adhere to the fingers or palm, yet it should retain the marks produced on it by the lines of the hand. An excess of water will cause stickiness, whilst too little water will produce a mass which will not properly take a clear impress of the fine lines of the hand. This method of determining the plasticity of materials by their 'feel' is satisfactorily employed by those who are continually handling clay, but it is unsatisfactory as a scientific test, as it introduces too much of the personal element, and the essential factors of pressure, changes of shape, and duration of pressure are not accurately defined. The same is true of the 'rolling-out test', in which balls of clay of a pre-arranged size or weight are rolled into strips of convenient size and then wound into a coil. The less plastic clays soon crack and may thus be distinguished from the more plastic ones. Strictly, this test depends more on the binding power than on the true plasticity of the clay. It may also be regarded as a measure of the consistency of a clay-paste.

(b) *Extrusion methods*, in which the clay-paste is forced by pressure through an

aperture and the quantity extruded is measured, are not really direct methods, for what they measure is the viscosity or flow and not the extent to which the shape of the mass has been changed, and this is an essential in the measurement of plasticity. However, a series of graphs, such as the one shown in Fig. VIII.24 may be very useful in comparing the yield points and secondary flow of several samples. A similar series compiled at different water contents, may also be informative.

(c) *Extension Methods.* Several investigators have suggested that either the amount or the rate of extensibility or the tensile strength of a paste are proportional to its plasticity. None of these is alone sufficient, but a useful and consistent figure may be obtained by multiplying the percentage of extensibility by the tensile strength of the material. Macey has pointed out the limitations which arise with this method as the result of shear hardening and induced dilatency.

Nevertheless the extrusion and extension properties of plastic bodies have such an important bearing on their behaviour in use that although tests of this kind may not give a true measure of plasticity, their importance should not be underestimated.

(d) *Compressibility methods* have been suggested which are based on the amount of pressure required to effect a definite change of shape or to deform a sample of a given size to such an extent that it cracks.

A method frequently employed is to apply a fixed load to a standard test piece and to measure the amount of deformation. The load may then be increased and the test continued until total failure occurs.

A simple means of comparing plasticities devised by McDowell¹ consists of a vertical rod mounted in guides so as to slide very easily up and down. The lower end of the rod has a flat plate attached and the upper end a similar, but larger, plate to support weights. A block of plastic clay precisely 2-inch cube is placed on the table, whilst the weighted rod is raised and then lowered gently on to the block of clay. After 30 seconds the height of the block is measured. The reduction in height is regarded as a measure of the plasticity. A weight of 2000 gm. is convenient. McDowell claims that this device gives much better results than the 'feel' of the paste and that more uniform manufacturing conditions can be obtained by it, particularly for clay-paste used for pressing.

Pfefferkorn² prefers to drop a known weight through a known height on to a cylinder of moist clay of known dimensions and to measure the deformation. Bowater³ modified the foregoing by allowing a known weight (2 lb.) to fall 6 inches on to a clay cylinder, 3 cm. diam. and 4 cm. high, and measured the additional distance travelled by the weight in compressing the clays. He passed the dry clay (or mixture) through a 20-mesh sieve, added water so as to produce a paste, plotted the 'deformed heights' of the test-piece against the percentage of water added to the dry clay, and found the resulting graphs to be all straight lines, but at different slopes and starting at different distances from the vertical axis. From these graphs he constructed a hypothetical curve (Fig. VIII.27) in which A represents the maximum water-content (r gm. per 100 gm. of dry material) for mixtures which theoretically suffer no deformation under the conditions of the test. B, with a water-content of

¹ McDowell, S. J., *J. Amer. Ceram. Soc.*, 11, 99, 1928.

² Pfefferkorn, K., *Sprechsaal*, 57, 297, 1924 and 58, 183, 1925.

³ Bowater, J., *Soc. Glass Tech.*, 14, 330, 1931.

R gm. per 100 gm. of dry material, is a theoretical point representing 100 per cent deformation. From this he concluded that the plasticity (P) may be found from the expression:

$$P = R(R - r)$$

The values obtained for $P \times 10^2$ place the various clays examined by Bowater in the same order of plasticity as that obtained by the customary method of 'feeling'.

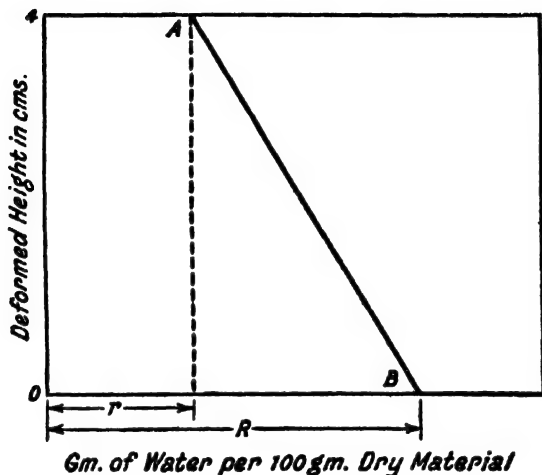


FIG. VIII.27. BOWATER'S PLASTICITY CHART

The value of tests based on measuring the plastic deformation under compressive forces has been increasingly recognised in recent years. Such determinations indicate the probable behaviour of plastic masses which are being shaped under pressure and they afford a rapid and reliable means of controlling the consistency of clay pastes. The term *workability* is widely recognised in the U.S.A. as implying the relative ease whereby plastic masses are deformed by pressure and it gives an excellent indication of plastic properties under practical conditions of moulding. The American Society for Testing Materials has adopted a standard procedure for measuring this property and such a method is of value for controlling the shaping or moulding of clay articles.

In the standard test (ASTM. Designation C.181-47) a test piece of 300 gms. is prepared by ramming the clay-water mass into a cylindrical mould of 2 in. diameter. The ramming operation is carried out by using a modified form of the sand rammer recommended by the American Foundrymen's Association.¹ The specimen is subjected to 10 blows on each end from a 14 lb. cylindrical weight and then extruded from the mould by means of a suitable plunger. The length of the test specimen is carefully measured, placed underneath the rammer and given three blows. The percentage deformation in length is the *workability index*.

¹ It is manufactured in Great Britain by J. Ridsdale & Co., Ltd.

The workability index is a good guide to the correct consistency of plastic masses for various methods of forming, and is much more rapid and precise than methods based on measuring the grading and the water content.

The following ranges of workability index have been found suitable in the manufacture of fireclay mixes:

<i>Method of Moulding</i>	<i>Workability Index</i>
Hand Moulding	35-50
Extrusion	28-34
Machine-made Bricks	15-25
Dry Pressing	5-8

The measurement of the workability index over a small range of moisture contents gives an indication of whether a clay is 'short' or 'fat'. If a change in the workability index from 25-35 is brought about by less than 1.0 per cent of extra water, the clay will be too 'short' for most practical purposes.

The measurement of compressibility is valuable especially when the clay being tested is to be moulded by high pressure methods. Such methods, however, are not fully descriptive of plasticity for they measure only the behaviour of a clay under the influence of compressive forces.

(e) *Shear and Torsional Methods.* In recent years, many attempts have been made to measure the plasticity of clay bodies using shearing or torsional methods. Talwalkar and Parmelee¹ subjected a clay bar to torsional stresses and plotted the stresses as ordinates and the angular strains as abscissae; the height of the curve above the x -axis is the yield point, whilst the length of the curve, and especially its upper terminal value, is taken as a measure of the amount of deformation the sample will stand without rupture. Parmelee and Rudd² have found that the point of fracture in a torsional test is too variable to be of use and that the slope-relations of the stress-strain curves must be considered. Wilson³ measured the stress developed in a solid cylindrical body when subjected to a twisting moment; Norton⁴ considers that a solid could not be in uniform shear throughout and for this reason prefers to use a tubular specimen although retaining the other essential features of the test.

The specimen is mounted in a torsion head, which is geared to a motor allowing various speeds of rotation. The stress developed is measured by the movement of an arm located on the specimen and recorded directly by a stylus on a smoked-glass plate. The torque in the specimen is plotted as a function of the angle of twist; a typical result is shown in Fig. VIII.28.

Three important characteristics of the curve are clearly shown:

- A. The yield point of the clay, or the limit of elastic behaviour.
- B. The maximum strength of the clay.
- C. The point of failure where rupture of the body occurs.

¹ Talwalkar, T. W., and Parmelee, C. W., *J. Amer. Ceram. Soc.*, **10**, 670, 1927.

² Parmelee, C. W., and Rudd, R. D., *J. Amer. Ceram. Soc.*, **12**, 14, 1929.

³ Wilson, E. O., *J. Amer. Ceram. Soc.*, **19**, 115, 1936.

⁴ Norton, F. H., *J. Amer. Ceram. Soc.*, **21**, 33, 1938.

The region between A and C is where the clay is subject to plastic flow and represents the degree of deformation which the body can undergo without breaking. Norton considers that both the *yield point* (which determines the force which the body can withstand without change of shape) and the *maximum extension* or *deformation* should be at a maximum in a plastic body. Thus, if the yield point is low, distortion or slumping may occur after the shape has been formed; a low extensibility indicates that the body does not readily mould, or has a short working range. An increase in yield point invariably results in a reduction in extensibility, but the

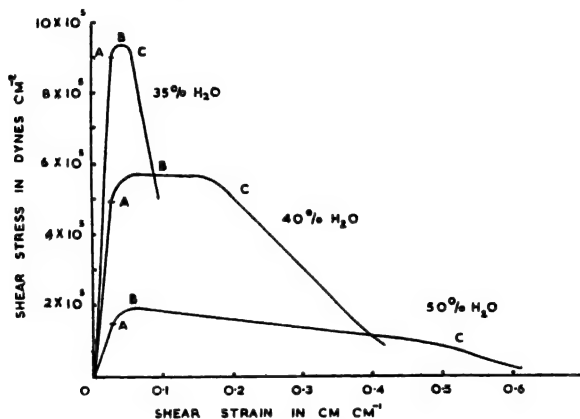


FIG. VIII.28.
THE STRESS/STRAIN RELATIONSHIP IN PLASTIC MASSES
(after Norton)

product of the two usually has a maximum at a particular water content. Norton defines this optimum value as the *maximum workability* point of the clay and Whittaker¹ uses such values as a basis of comparison for the *plasticity* of various clay fractions.

Although such a method of measurement gives a useful indication of the working range of clay bodies, there are many factors which influence the results. The time through which the shearing force is applied may influence considerably both the yield point and the extensibility. Thixotropic and dilatent materials often show anomalous behaviour which may give rise to misleading conclusions.

Various other methods have been suggested which are claimed to measure plasticity. Linseis,² for example, considers that a useful index is given by recording the tensile breaking strength as a function of the resistance to extrusion ('shear resistance') at different water contents. Other workers confuse binding strength, adhesion, bending moment and other physical properties with true plasticity.

Although the work of Macey, Norton and others has contributed much to the knowledge of the many factors which influence plasticity, it has also indicated that

¹ Whittaker, H., *J. Amer. Ceram. Soc.*, 22, 16, 1939.

² Linseis, M., *Sprechsaal*, 84, 259, 1951.

one single experimental technique cannot be fully descriptive of this property. This may not be as serious a disadvantage as it appears to be, for in clayworks practice it is seldom necessary to know the full range of plastic behaviour. One aspect or associated property usually predominates and the measurement of this single feature is often a simple matter and gives results which are ample for technical control.

PROPERTIES ASSOCIATED WITH PLASTICITY

THE many misconceptions of the nature of plasticity have led to numerous unsound conclusions, and many investigations of the effects of various substances on plasticity have been rendered nugatory because the results have not been correlated to plasticity, but to some other property mistaken for it. Some of these mistakes have been described in the section on the Measurement of Plasticity, whilst others are referred to in the following pages.

Stickiness. When even a small proportion of water in excess of that required to develop the maximum plasticity is added to a clay-paste, the mass adheres to the fingers and becomes 'sticky'. The proportion of water required to create this condition in a clay is a measurement of definite physical significance and is one of the important 'constants' of clays. Its determination is easy to those accustomed to working clay-pastes, but not to others, and for this reason many chemists and physicists have failed to recognise its value.

The *sticky-point* is defined as that at which a clay-water mixture contains so much water that it begins to adhere to the fingers, whereas the same material with a slightly smaller proportion of water will show imprints of the fine lines of the skin, but will 'come away' cleanly. This critical change in the behaviour of clay-pastes has long been known to potters and other clay workers, but it was F. Hardy¹ who made it popular among chemists by regarding it as indicating the maximum imbibitional capacity for water of the colloidal material in clay.

Keen and Coutts² have shown that the sticky-point is directly proportional (though only roughly) to the clay-content of a clay which has been treated with hydrogen peroxide so as to remove humus (by oxidation). Keen has also stated that 'there is good reason to suppose that the sticky-point value represents the sum of (a) water held in the interstices of the clay, and (b) water held by the colloidal material (organic and inorganic) in the clay'.

It may be measured by converting the clay into a sticky paste (avoiding the use of more water than is necessary), then weighing the mass before and after drying at 110° C.

Some clays are naturally sticky rather than plastic, as, for example, those found in the geological formation known as 'London clay'. They can be used industrially only when too little water is present to develop their plasticity fully, or by adding a non-plastic material so as to lower their plasticity. Such clays often show a pseudo-plasticity (p. 479).

Mobility. The term *mobility* is used to indicate 'ease of movement'; it is

¹ Hardy, F., *J. Agric. Sci.*, 18, 740, 1928.

² Keen, B. A., and Coutts, J. H. R., *South African J. of Sci.*, 27, 182, 1930.

applicable to solids, liquids and gases and, in the case of liquids, it is synonymous with fluidity.

The mobility of a clay or clayey paste depends on its plasticity and on the extent to which the solid particles are separated by water. If the plasticity is low, or if sufficient water is not present, the material will be largely immobile, but a highly plastic paste, or one containing a large proportion of water, is readily mobile. In the case of a plastic paste, pressure is required to make the material move, but a slip is as mobile as any fluid of the same character. As the mobility is not strictly proportional to the percentage of water present, it is not desirable to include in any mobility-coefficient an expression for the water present in the mass. In other words, the mobility should be determined on an actual sample and either its consistency or the percentage of water in it should be stated quite independently of any figure for the mobility.

The mobility of a clay slip is the converse of its viscosity (see p. 449).

Extrudability. Closely allied to the mobility and viscosity of a clay paste is the facility with which it can be made into certain useful shapes by extrusion through a die or mouthpiece, as in the manufacture of wire-cut bricks, pipes, etc. In order that the extruded products may be commercially useful, the material to be extruded must be plastic as well as mobile, so that no simple factor can be used to express its extrudability. Probably the simplest mode of expression is in terms of viscosity, i.e. in the ratio between the quantity extruded in unit time and the pressure required to extrude; but the size and shape of the aperture have so important an influence that it is almost impossible to reduce the idea of extrudability to simple terms. In practice, the relative extrudability of various clay pastes must be expressed in terms of viscosity, the shape and size of the aperture being strictly defined. Thus, a paste which is quite satisfactory for the production of bricks by extrusion may be almost useless for the production of pipes or blocks of special shape by the same process.

Binding Power. The binding power of a clay is measured by the amount of non-plastic material which can be incorporated without the plasticity of the mixture being reduced below that which is necessary for good modelling or moulding properties.

The binding power of a clay must not be confused with its plasticity, however, as these are quite distinct properties, though, as both are dependent on the nature and proportion of the colloidal gel matter present, they are, to some extent, related to one another. Thus some highly plastic clays have a high binding power, but other clays have a high plasticity and a comparatively low binding power.

The binding power of a clay is analogous to the property possessed by various colloidal gels of retaining particles in their mass in a state of suspension. It appears to be due almost wholly to the viscous liquid constituent of the plastic paste, but the amount of non-plastic material which can be incorporated with any given clay is limited by the amount of such material already present. For this reason, any treatment which increases the proportion of viscous material in the mass also increases its binding power.

The chief effect of water on the binding power of a clay, is to increase the volume of the colloidal gel matter present and, therefore, to enable this matter to

cover a large surface of inert material. In this way, the addition of a suitable proportion of water, acting through a sufficiently long time, will increase the actual (though only to a minor extent the potential) binding power of a plastic clay.

The binding strength of clays is dependent on many factors although the surface area, or amount of colloidal fraction, is probably the most important. Thus montmorillonite clays are superior to those of kaolinite type as shown in Table VIII.VI.

TABLE VIII—VI. THE BONDING
STRENGTH OF CLAYS

<i>Clay type</i>	<i>Cross breaking strength (gms. per sq. cm.)</i>
Kaolinite	200–250
Fireclays	150–450
Ball clays	400–580
Bond clays	600–800
Montmorillonite	1500–2500

Clays, such as ball clays, with a high binding power are very valuable in the manufacture of articles containing, by necessity, a large proportion of non-plastic grains, as grog bricks, porcelain, earthenware and various refractory articles of special kinds. Bonding clays (such as bentonites) which, in general, give a higher wet and dry strength than ball clays, are used in the manufacture of sand moulds for steel castings.

The binding power of clays may be manifested in both the wet (or *green*) state and in the dried material. It is usually measured by determining the breaking (either compressive or tensile) strength of standard-sized blocks made up of various small proportions of the clay with a standard sand, after mixing with various amounts of water.

The *green strength* of clay/sand mixtures resembles plasticity in that a maximum value is recorded at a certain moisture content and, as a result, some writers confuse the two properties and define plasticity in terms of maximum wet strength. For the reasons given previously this is incorrect because binding strength is but one aspect of plasticity.

Grim and Cuthbert¹ have investigated the bonding action of clays in wet sand mixtures. They conclude that the water molecules are associated with the clay mineral particles which, in turn, coat the surface of the sand grains. Furthermore, they claim that the maximum green strength is developed when the adsorbed water molecules are in a rigid condition induced by the surface structure of the clay minerals themselves.

Ideally, a thin film of clay is thought to cover each sand grain and when maximum green compression strength is developed a definite layer of water is associated with the surface of the clay mineral flakes. With montmorillonite-type clays, the water film thickness at maximum strength is about three molecules or 8 Å thick and is fairly uniform throughout the mass, but clays of the kaolin or illite-type are believed to form irregular coatings made up of large clay aggregates formed around the sand

¹ Grim, R. E. and Cuthbert, F. L., *Illinois State Geol. Survey*, No. 102, 1945.

grains. In both cases, the clay mineral films run into each other and form *wedge-blocks* which unite adjacent sand particles.

In the 'wedge-block' theory the water molecules are considered to have a rigid structure which is continuous throughout the mass. Grim and Cuthbert favour the concept of a type of ice structure being developed. Although this theory adequately accounts for the concept of green strength in clay/sand mixtures, several objections have been advanced. Macey, for example, has pointed out that Grim and Cuthbert assume that all the water present is associated with the clay and the possibility of some filling the capillaries has been ignored. It may further be argued that under the conditions of mixing, water molecules would be unlikely to penetrate between all montmorillonite flakes and give a uniform layer. The concept of a virtually continuous clay film with wedge-block linkages is, however, most valuable and explains many of the features of this type of bonding.

Organic Bonds for Clays, etc. Organic bonds or *binders* have been added to clays since remote times—gum arabic is added to porcelain and bone-china bodies to increase the plasticity and facilitate the production of delicate porcelain baskets, flowers, etc.

In the manufacture of refractory bricks made largely of non-plastic materials, about 2 per cent of sulphite lye (a by-product of the paper industry) is used as a binder. It is also used in the United States in the manufacture of some shale-bricks.

Organic binders are used much more extensively in the United States than in this country. The most important ones are:

(a) Flour and starches, which are cheap but do not appreciably increase the plasticity.

(b) Gums—gum arabic, gum tragacanth, gum acia, dextrin.

(c) Alginates—made from seaweed—effective but too expensive except for special wares.

(d) Polyvinyl and other alcohols and water-soluble resins.

(e) Silicon esters (silicones) which are organic compounds of silica.

(f) Methyl ethyl cellulose, sodium carbomethyl cellulose and other cellulose compounds.

(g) Casein-glue, glue and gelatin—chiefly used for binding glazes.

(h) Water soluble paraffin waxes—chiefly used for small steatite goods.

(i) Waste oil-residues, tar, pitch, etc.—used chiefly for firebricks of special shapes.

All these binders create only a *pseudo-plasticity* and they are quite distinct in their nature and action from bond clays and plastic clays.

INDUSTRIAL APPLICATIONS OF CLAY/WATER SYSTEMS

1. SLIPS, SLURRIES AND SUSPENSIONS

THESE are prepared by mixing the solid materials with a suitable proportion of water so that the body has fluid properties and will flow under its own weight. They are used for various purposes, the most important of which are:

- (a) To ensure a more thorough mixing of ceramic materials than is possible when they are mixed in a dry or plastic state.
- (b) To enable the materials to be applied more easily than would otherwise be the case, as in coating ware with an engobe or glaze or in decorating ware by painting.
- (c) To enable articles to be made by the process known as casting (p. 493).
- (d) To effect the purification of clays and other ceramic materials.
- (e) To enable pottery scrap to be re-used.

Homogeneous mixtures of ceramic materials are best prepared by mixing the dry substances in suitable proportions, soaking the mixture in water until it is thoroughly slaked, and then stirring mechanically until it is of uniform consistency throughout. An alternative method, which is often preferred, consists in making each solid constituent into a separate slip, which is then passed through a sieve in order to separate undesirably coarse material. The consistency of each slip is then adjusted so that it has a definite 'weight per pint' (p. 407). The slips are afterwards mixed in suitable proportions when required. This method ensures the better soaking of the solid materials and the removal of coarse matter before the proportions of the various materials are measured and so leads to a superior product. If the mixed materials are to be converted into the form of a paste or powder, the excess of water may be removed by means of a filter-press or by evaporating the water by means of heat, or by a combination of these methods. When a slip contains only a small proportion of solid matter, a large part of the water may sometimes be removed by allowing the slip to 'settle' for some time and then running off the clear supernatant water; the objection to this method is that the heavier and denser particles of solid matter may settle first and so cause an undesirable amount of 'un-mixing'.

This method of preparing pastes is largely used in the manufacture of fine earthenware, porcelain, etc., as it ensures a product of much greater homogeneity than any other method. Its chief drawbacks are its cost and the necessity of increasing the compactness of the paste by a further treatment in a pug-mill or other machine.

Slips for engobes and glazes are prepared by mixing the various solid materials and water as described above, and the slip is then applied direct to the ware by dipping, painting or spraying. The slips are generally made up to a definite weight per pint, as this is a convenient means for measuring the amount of solid matter they contain.

Table VIII.VII shows the proportion of solid matter and water in slips in common use in the Potteries.

Adequate *control of the viscosity* of glazes and enamels is very important as it affects the amount retained on the surface of the ware and also the manner in which the surplus slip drains away—too viscous a slip will leave tear-drops or lines and too fluid a slip may drain off to such an extent as to leave too thin a coating on the ware. When glazes and engobes are applied by brushes the correct viscosity is particularly important as a means of preventing bubbles being formed during the brushing: these may later form pinholes in the ware.

One means of controlling the viscosity is to add a suitable proportion of a colloidal material. Clay is very suitable, but it may increase the temperature at which

TABLE VIII—VII. SLIPS USED BY POTTERS

	<i>Standard slip weight oz. per pint</i>	<i>Weight of solid per standard pint</i>	<i>Weight of water per standard pint</i>	<i>Solid matter per cent</i>	<i>Water per cent</i>
		oz.	oz.		
Earthenware body	35	24.20	10.80	69.15	30.85
(Casting slip)	36	25.81	10.19	71.68	28.32
	37	27.43	9.57	74.14	25.86
Ball clay (mixed)	24	6.70	17.30	27.91	72.09
China clay (mixed)	26	9.75	16.25	37.50	62.50
Flint slop	31	18.16	12.84	58.58	41.42
Cornish stone slop	31	17.57	13.43	56.69	43.31
Earthenware glaze	33	19.96	13.04	60.48	39.52

the engobe, glaze or enamel matures and the necessary adjustments may be troublesome. Bentonite is increasingly used for this purpose, the viscosity being controlled by the subsequent addition of a solution of calcium chloride. Instead of clay, 1-5 per cent of starch, dextrin or gum (previously dissolved in hot water) may be added to the slip.

Thixotropy (see p. 444) is an important consideration in glaze and engobe slips. Suspensions which have this property thicken or gel on standing, but when they are stirred free-flowing conditions are restored. Some degree of thixotropy is an advantage in slips especially when heavy or large particles are present which would otherwise tend to settle out on standing. The structure which develops within such suspensions is strong enough to prevent sedimentation yet, when stirred, the slip may be readily transported through pipes or poured into moulds.

Beech and Francis¹ have demonstrated that a thixotropic glaze does not 'run' from sharp edges of ware and yet is sufficiently free-flowing to penetrate all recesses.

Thixotropic bodies are liable to develop faults, however, which arise principally from the large amount of contained water, which leaves air spaces on drying out; 'pin-holing' and similar faults are, in some cases, attributable to this reason. The sedimentation density of slips is drastically reduced when thixotropy is present. In order to induce sufficient thixotropy in slips, a small amount of colloidal material is occasionally added and for this purpose a small percentage of bentonite is extremely effective.

To produce the most satisfactory slip from suitable raw materials, a compromise in properties is usually necessary. Ideally, a slip should contain the maximum amount of solid matter consistent with a good flowability. In attaining this, the thixotropy invariably reaches unworkable proportions—the slip 'solidifies' if not kept constantly stirred, draining of moulds becomes difficult and the cast body shrinks excessively on drying.

The best compromise between a high slip density and a low thixotropy is usually secured in practice by using a mixture of sodium carbonate and sodium silicate as deflocculant; the former is an excellent dispersant whilst the latter inhibits thixotropy.

¹ Beech, D. G. and Francis, M., *Trans. Brit. Ceram. Soc.*, 44, 25, 1945.

The most suitable amounts and ratio of the two electrolytes can be determined only by experimentation.

The consistency of a slip is dependent on numerous factors, although the amount of colloidal material present is the chief determinant. Consequently the viscosity will be related to the degree of flocculation. Should the required slip be too viscous for pouring, the addition of deflocculants or electrolytes may be of value; on the other hand an increase in viscosity may be effected by adding small quantities of flocculants such as hydrochloric acid, or a salt in which the acid radicle predominates, e.g. zinc chloride, stannic chloride, aluminium chloride or calcium chloride.

Many factors influence the viscosity or 'flowability' of clay slips, and every clay or mixture has its own characteristics and the correct conditions for a suitable slip can be found only by experience. Many of the problems in making-up a clay slip are related to the ease of dispersion of the clays being used—a factor which is often overlooked. The dispersion of prepared china clay and ball clays is a relatively simple matter and provided that slips containing these materials are adequately blunged, the correct consistency is easy to secure.

In the slip-casting of earthenware and stoneware bodies, however, shaley clays are frequently employed and the breakdown of these materials is often difficult and seldom complete after long periods of blunging. The degree of weathering of such clays is of great importance and casting slips made from materials which have had different treatments, may vary considerably in consistency and other properties.

To secure adequate control over a casting slip, the clays must be at maximum dispersion which may be secured by:

- (i) Using only well-weathered clays.
- (ii) Grinding the clays and other raw materials as finely as possible prior to use.
- (iii) Blunging vigorously and for a long period. Hot water may be used with advantage in the dispersion of some clays.
- (iv) Ageing the suspension before use. Some firms allow their slips to stand for a week or more.

It is well-known that some slips are considerably improved by additions of weak acids and for this reason humic or tannic acid is often added in small amounts. Although such materials are known to form protective colloids and so assist in the deflocculation of some clays, sulphuric and hydrochloric acids are also beneficial in some cases and their action must be quite different. Shaley clays frequently break down more readily in an acid solution and their value in casting slips can be enhanced by blunging them, prior to deflocculation, in water to which has been added a small amount (about 0.1 per cent is usually sufficient) of sulphuric or hydrochloric acid.

The dispersion of a clay and the consistency of a slip may be improved by passing it through a fine sieve or lawn after blunging.

The *slip-casting process* (Fig. VIII.29), consists in pouring a suspension of suitable composition and concentration into a preshaped plaster mould, the highly porous nature of which removes water from the slip mainly by capillary action. In the neighbourhood of the plaster wall the suspension becomes locally concentrated and a type of skin formation develops. It is not unlikely that flocculation of the suspension occurs at the surface of the mould due to the exchange of soluble

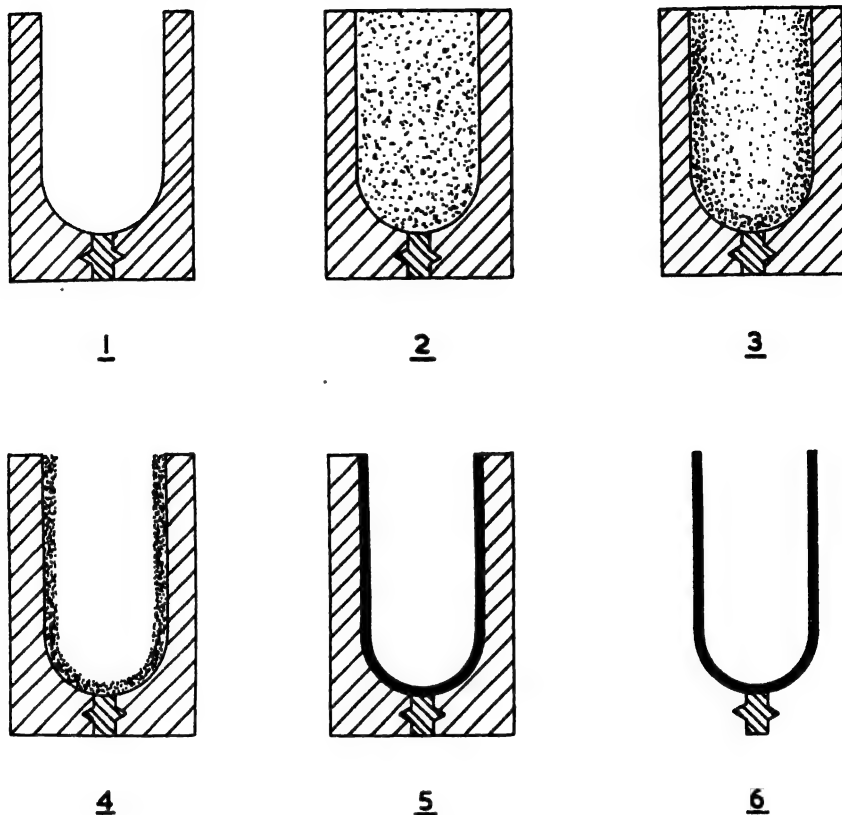


FIG. VIII.29. STAGES IN THE SLIP CASTING PROCESS

- | | |
|-------------------------------|--|
| 1. The prepared plaster mould | 4. The 'skin' remaining after emptying the mould |
| 2. The mould filled with slip | 5. The dried 'skin' |
| 3. The formation of a 'skin' | 6. The article removed from the mould |

calcium ions which would considerably assist localised flocculation in a dispersed clay.

The longer the slip is left in the mould the more water is removed and the 'skin' or compacted layer becomes thicker. The process can be stopped at any time by pouring off the excess liquid, or alternatively, more slip may be added to compensate for the water removed, until such time as the complete space within the plaster mould is filled with a solid concentrate. The former process is termed *drain casting* whilst the latter is known as *solid casting*; both methods are used although the former is more frequently employed. Provided that a suitable suspension is prepared, slip casting requires very little skill and yet by its use, articles of complex shape and with extremely thin walls may be produced. It is, therefore, a very valuable method for the manufacture of articles of fine earthenware, porcelain, etc. The method is finding increased application in many ceramic processes where a homogeneous material

is required from fine-grained components. Similarly, large thin-walled objects such as crucibles, retorts and sanitary ware are often made by these methods.

Refractory tubular ware is made by spinning a slip inside a cylinder of the required diameter. The suspended particles sediment round the walls by virtue of the centrifugal force and the excess water may be removed by passing a current of warm air through the inside of the mould.

In the drain-casting process, the time required for a slip to remain in the mould before the surplus is poured off varies according to its nature. A slip made without any added electrolyte may require several days, but if a suitable amount of alkali is added the time is considerably reduced. If ware with very thick walls is made by this process, a long time is essential even in the presence of an electrolyte. Thus, in the manufacture of gas retorts, a period of fifteen to twenty hours may be necessary. When a vacuum mould is used, as suggested by B. J. Allen, much less time is required, as the water is absorbed more rapidly by the mould.

The rate of 'skin-formation' is related to the properties of the suspension and many casting difficulties arise through lack of careful control. The sedimentation volume and the solid concentration of the 'skin' are subject to considerable variation, due, in the main, to suspension conditions. Very little work has been done on this perplexing problem but one cause of poor casting quality is structure formation or advanced thixotropy which develops as the suspension begins to concentrate. This can be minimised by ensuring that the electrolyte added to increase fluidity is not present in excess. In other cases, the initial 'skin' is so dense that water cannot readily penetrate it and the increase in layer thickness is exceptionally slow.

The Mechanism of Slip Casting. Although there has been much speculation as to the factors which govern the formation of a 'skin' when a slip is cast in a plaster mould, there is very little reliable information whereby a safe prediction can be made.

It is now generally accepted that the principal mechanism in 'skin' formation is the simple physical reduction in the water content of the slip near to its contact surface with the plaster. The rate of development of the rigid layer proceeds at a uniform rate which suggests that the rate of removal of water is the all-important factor.

Hind¹ demonstrated that the solid layer during casting increased in thickness at a rate which was dependent on the following factors (a) the permeability to water of the cast layer or, in other words, its filtration rate, (b) the specific gravity of the slip and (c) the suction pressure of the mould. If these were maintained constant, Hind showed that the thickness of the solid layer could be related to the square root of the casting time.

Carman² applied the Kozeny equation to the slip casting process and assuming that the mechanism is simply one of dewatering he deduced the equation

$$\frac{L^2}{T} = \frac{2PE_g^3}{5S_p^2\eta(y-1)(1-E)^3}$$

¹ Hind, S. R., *Trans. Eng. Ceram. Soc.*, 22, 90, 1923.

² Carman, P. C., *Trans. Inst. Chem. Eng. (London)*, 16, 168, 1938.

where L is the thickness developed in time T , P is the suction pressure, E is the percentage of voids in the cast; η is the viscosity of the fluid; S_p is the specific surface area of the solids and γ is the volume concentration of the slip.

The filtration rate of the solid layer is governed principally by the proportion of fine-particled material in the slip but Kocatopcu³ has shown that the packing of the particles and the ratio of plastic to non-plastic components are also important.

The nature of the plaster mould is known to influence the casting rate; the finer the capillaries the greater will be the suction pressure and hence the more rapidly will water be withdrawn.

The condition of the plaster is another influencing factor, a dry mould is more effective than one where the initial water content is high.

In preparing a good casting slip and a good product from it, the following are essential:

- (i) Carefully selected and prepared clays and non-plastic materials.
- (ii) The correct proportions of each component.
- (iii) A minimum proportion of water.
- (iv) The appropriate type and amount of electrolyte as a deflocculant.
- (v) The best consistency in the slip.
- (vi) A suitable mode of preparation and an efficient method of control.
- (vii) A well-prepared mould (usually made of plaster of Paris).
- (viii) A suitable time in the mould.
- (ix) A controlled temperature during casting.

To secure the best results in casting, it is necessary to use a *suitable combination of materials* so as to produce a moderately plastic material of sufficient binding power. Slightly plastic materials are preferable to highly plastic ones, as they require less alkali to maintain a suitable fluidity and the articles can be more readily removed from the moulds. Clays are frequently added to fine-grained components which in themselves are not sufficiently plastic to produce a strong cast. *China clay* and *kaolins* produce a very porous product when cast, but they have not sufficient binding power to produce a strong mass. *Ball clays*, on the other hand, have the requisite binding power and increase the fluidity of slips, but give too dense a product, which makes it very difficult to secure the formation of a sufficiently thick layer in the mould. Ball clays are deflocculated at a low P_H (on the acid side of the neutral point), but have a higher absorption factor, whilst china clays deflocculate at a higher P_H (on the alkaline side), but have lower absorption power, i.e. there are opposite effects and the amount of alkali required does not depend on a single factor. For these reasons, the proportion of ball clay should not exceed 20 per cent of the body, and a large excess of china clay should be avoided. Fireclays vary in their properties in accordance with their nature, but are usually intermediate between kaolins and ball clays.

In mixtures of several materials, serious segregation of the components can take place during casting. As water is drawn through the compacted layer to the mould surface, finely-grained components such as clay may be transported and deposited near to the wall of the mould, so that the external layers may have a much greater

³ Kocatopcu, S. S., *J. Amer. Ceram. Soc.*, 29, 99, 1946

concentration of such material than those in the interior. The physical properties of the two regions may be so different that differential shrinkage, during drying and firing, may lead to failures.

The *proportion of water* in a slip used for casting should be as small as possible so as to avoid undue shrinkage of the ware. In estimating the amount of water required, it is necessary to use only dry materials or to take into account the moisture contained in the raw materials. The use of *hot water* is sometimes advantageous.

The fluidity of a slip is largely dependent on the degree of deflocculation, hence the addition of a *small amount of electrolyte* may considerably reduce the amount of water required to produce a fluid suspension. The addition of about 0.25 per cent of sodium silicate or of soda ash, or a mixture of these two substances, will increase the mobility of a slip weighing about 36 oz. per pint to that of an untreated slip weighing only about 26 oz. per pint. If no deflocculant is used, most dry clays will require almost an equal weight of water to convert them into a slip, but with a deflocculant good slips may usually be produced, which contain only about 15–25 per cent of water. Non-plastic materials may usually be made into dense slips by the aid of a deflocculant; thus, slips for casting zirconia crucibles may weigh about 30 oz. per pint.

Various deflocculants for clay have been described on page 443, but all are not equally suitable. Sodium carbonate or sodium silicate, or a mixture of these two, are usually the most satisfactory, but when sodium carbonate alone is used a high surface tension is produced and the solid particles tend to 'ball up' and cause the entanglement of air bubbles. Sodium silicate alone, on the other hand, tends to produce a 'stringy' slip and it does not hold the clay in suspension so well as sodium carbonate. If only a single electrolyte can be used, sodium carbonate appears to be the best. Sodium hydrate is much more active than sodium carbonate and silicate, but it is not used to any great extent partly because of its corrosiveness. Sodium carbonate (soda) alone produces a slip with a tendency to be thixotropic.

For the reasons given earlier in this chapter, the presence of soluble salts may interfere with slip formation. Such an example is calcium sulphate which is so undesirable that it may be necessary to pretreat the suspension water with a solution of a barium salt to ensure its complete removal.¹

The proportion of deflocculant which is the most suitable for any given purpose must, of course, be found by trial. The effect of electrolytes on a ceramic slip may be determined by blunging together definite quantities of the clay or other solid material and water with different proportions of various electrolytes for a period of about two hours. The resultant mixtures are allowed to remain at rest for a suitable time and are then examined. The resulting slip which most closely corresponds with what is required is then noted.

The *correct consistency* in a slip is a major factor in promoting good quality castings. If the slip is too thick, it does not flow readily and imperfections may occur especially if the mould is of complicated shape. A thick slip does not drain successfully and forms a loose-textured 'skin' which is uneven and has an excessive drying

¹ When scraps of broken articles are to be included in the casting slip, it is particularly important to remove (or render harmless by adding barium chloride or carbonate) any calcium sulphate derived from the moulds.

and firing shrinkage. A slip which is too thin in consistency is slow to form a 'skin' of the required thickness and the coarser material tends to settle, thereby producing an uneven body.

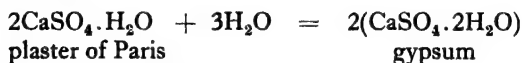
Although not always realised, the *mode of preparation* of a slip influences its casting properties. The clays and other body materials should always be added to the water and not vice versa. It is equally necessary to use all the water required at once and not in successive quantities. If the latter procedure is adopted, 10–25 per cent more water will be needed, and the slip will be of inferior quality. *Air-bubbles* in slips may cause several serious kinds of defects in the goods, including pin-holes and blisters. They may be avoided by care in mixing (blunging) the various materials with water and may be removed by treating the slip under reduced pressure or even by prolonged storage.

In making slips of various materials it is most important that they should be added to the required amount of water in the following order: (a) deflocculant (if any); (b) clays; (c) non-plastic materials. This procedure is necessary because when all the materials are added at once an excessive quantity of water is required.

Control of the casting-slip is usually effected by determining (1) the 'weight per pint' (p. 407) or the specific gravity at which satisfactory results are secured, (ii) the viscosity of the slip, or (iii) measuring the rate of 'skin-formation' in the mould.

In accurate work it is necessary to determine both the viscosity (p. 454) of the slip and its 'weight per pint' or specific gravity, as these two properties are not necessarily related. If the viscosity is too low, partial settlement of the suspended matter will occur and may spoil the goods.

The *composition and manufacture of the moulds* into which the slip is cast are of great importance. The material most commonly used is plaster of Paris which has the property of combining with water to form needle-shaped crystals of gypsum which interlock and intergrow to form a strong yet porous mass. The reaction may be simply represented as:



A mould must have the following properties:

1. Sufficient mechanical strength to withstand the weight of added slip.
2. Perfection in construction so as to give faithful reproducibility in the cast ware.
3. A smooth interior surface finish to avoid imperfections and irregularities in the final shape, particularly at the joints.
4. Sufficient porosity to allow for the rapid removal of water yet with a pore size small enough to prevent penetration of the casting-slip itself.

A plaster of Paris mould is prepared by mixing the finely-powdered raw material to a thick slip with water, pouring it around a former, model or pattern of the desired shape and then allowing the paste to set. The slip must be of a consistency suitable for pouring and, at the same time, the concentration must be high to give a dense hard set. Normally plaster of Paris will stiffen rapidly when mixed with water, although the rate may be influenced by the addition of suitable salts. Borax is of

value as a retarder, whilst potassium sulphate or Rochelle salt increase the rate of setting, but reduce the overall shrinkage. Borax is a common addition to pottery plaster, for by its use a more concentrated slip can be made up without undue hastening of the setting time.

In practice, concentrations of up to 66 per cent plaster to water are used for making moulds, although greater dilution may be necessary if a complex shape has to be reproduced.

Plaster moulds are used in dentistry both for casting porcelains and for fabricating metal insertions. In the latter case particularly, the large contraction of the metal on cooling is troublesome and it is not possible to reproduce faithfully the required shape by using normal plaster moulds. Some thermally-expanding material is normally added to the plaster before the mould is made which causes an increase of the internal dimensions when molten metal is added. If the mould mixture is adjusted correctly true compensation for the contraction of the metal shape can be made. Both cristobalite and quartz are used for this purpose and the required amount to be added to plaster must be determined experimentally for a particular metal or alloy.

The number of re-entrant angles in the shape to be cast complicate the slip process. Where these occur, the mould must be made in several pieces to facilitate the removal of the finished cast. Thus, the mould for a complex shape may be composed of many parts, each of which has to be placed into position before the clay slip is added.

The *best length of time in the mould* can be found only by trial; too short a time will produce thin-walled and weak ware; an excessively long time is uneconomical and may produce over-thick ware, but otherwise does little harm.

The *temperature during casting* is important as it affects the stability and viscosity of the slip. A temperature range of about 5° F. is permissible but a larger range may yield irregular results.

Improving and Purifying Clays. As the particles of clay minerals are much smaller than those of most others in commercial clays, a considerable amount of improvement and purification can be made by converting such clays into a slip and then passing it through a fine sieve. A still further purification can be obtained by allowing the slip to rest and then pouring off the liquid (which will contain most of the 'true clay') and leave most of the impurities behind as a sediment. The slips must be dilute and for adequate purification the second slip must not usually contain more than 5 per cent of suspended matter; stronger slips should be diluted with water to ensure this.

Clays are frequently pretreated before being used as casting-slips. It is common practice to purify them although this may involve nothing more complex than the removal of coarse or large-sized particles.

Considerable commercial and technical advantages may be secured by making use of the colloidal properties possessed by clays, by means of which they can be suspended in a much smaller proportion of water and yet effectively separated from other (non-colloidal) materials which cannot be so readily suspended. To effect the purification of clays by this means, use is made of the fact that clays, like other colloidal materials, can be dispersed (see p. 439) by means of a suitable electrolyte,

and when so dispersed or deflocculated they remain permanently in suspension until their state is changed (by the addition of a coagulant or flocculating agent); the principal impurities found in clay, such as quartz, mica, feldspar, pyrites, calcium carbonate, and various iron compounds, are not so affected. Consequently when stirred well with alkaline water, these impurities remain suspended for only a short time and soon settle out, so that the purified clay suspended in water may readily be removed by decantation.

There are many deflocculating agents which are effective and the most suitable for any particular clay can be found only by trial and error.

An alkaline salt is the most suitable and sodium phosphate, silicate and carbonate are in general use. The amount added is usually small and invariably less than 7 lb. per ton of dried clay.

The separation process is best carried out in large tanks which permit the free sedimentation of the coarser grains. The separation of the clay from the greater part of the impurities is fairly sharp, provided that a suitable proportion of deflocculant has been added, but extremely small particles of silica and colloidal components cannot be removed. The chief difficulties connected with the process are found when it is required to separate the purified clay from the water in which it is suspended. To effect this, four general methods are available:

1. *Removal of the water by evaporation*, usually by the aid of heat. This is very effective, but usually too costly. It also causes any soluble salts in the water to remain in the clay. Where waste heat is available, this method is still worth consideration. Care must be taken not to over-heat the clay or its active properties may be destroyed.

2. *Filter-pressing*.

3. *Flocculation or precipitation* of the suspended clay particles by the addition of acids or other electro-negatively charged substance.

Any of the flocculants mentioned on page 478 may be used though the most convenient are hydrochloric acid, acetic acid, aluminium sulphate or aluminium chloride. Sulphuric acid has also been used for this purpose, but it has the serious disadvantage that, when the clay is afterwards dried by artificial heat, the sulphuric acid chars any organic matter present and so spoils the appearance of the clay. The only disadvantage of the use of a flocculant is that any colloidal impurities present or any impurities which may be adsorbed will contaminate the clay.

4. *Electro-osmosis* (p. 506), i.e. by the use of a current of electricity to separate the water and suspended matter. This method is interesting as it can simultaneously effect a further slight purification, especially from iron compounds, but it is very costly. Details of the method are to be found in *Modern Brickmaking* by A. B. Searle.

Various statements have been made from time to time to the effect that crude clays may be purified by electro-osmosis. This is scarcely correct, because the electro-osmosis does not, in itself, effect the chief separation of the impurities from clay, but only separates much of the water. The finest particles of the most important impurities, such as quartz, mica, feldspar, etc., bear the same electric charge as the clay particles and so cannot be completely separated, though some oppositely-charged impurities may be separated by electro-osmosis. Under normal working

conditions the greater part of the impurities is separated by deflocculation and settlement before the material enters the osmose machine, so that the latter is more correctly to be regarded as a drying device with a slight purifying action. Schwerin's process is no cheaper and no more efficient than the filter press except for very fine clays as so little purification is due to the different velocity of clay and the impurities under the influence of the electric current.

5. *Centrifugal action* may be employed to separate particles of almost any size, as it has a force which can be made a thousand times as great as that of gravity and can be varied within narrow limits. Centrifugal force is largely used in the scientific investigations of the properties of clays in suspension (see Chapter VII).

2. PASTES AND PLASTIC MASSES

FOR the manufacture of bricks and most solid ceramic bodies, the raw material usually contains insufficient water to allow free flow and the mass is moulded to the shape required by the application of pressure. The amount of mixing water varies and is dependent on the nature and complexity of the shape to be made and the raw material employed.

The shaping of plastic masses involves applying a pressure to cause the body to flow until it fills the required mould. By this means the particles of the body are compressed and packed together by the external pressure which is applied, either by hand or by power, to the mass.

As considerable movement of material has to occur it is to be expected that less pressure will be required to form a material which is capable of easy flow than one in which movement is restricted. An agglomeration of spherical or rounded particles will, for this reason, be shaped or formed more readily than one composed of angular fragments.

Plastic masses, or those in which the water content is high, are easily moulded by pressure, because the moisture behaves as a cushion or lubricant and permits free flow. A drier mass does not flow so readily, hence higher forming pressures are necessary.

The shaping of bodies composed of plate-like particles is further complicated because the individual grains become orientated and offer increased resistance to the applied force (see Fig. VIII.30). Particle orientation is most likely to occur when the water is present in large proportions and when a considerable amount of displacement takes place on the application of the forming pressure. A body so prepared is frequently laminated and may develop cracks and fractures during drying or firing.

A manufacturer has, therefore, to effect a compromise; a mass with a high water-content can be shaped under a low pressure but gives a less dense body with a tendency towards laminations; a drier material will pack tighter and with less particle orientation, but only on the application of a much greater pressure. The various methods of moulding used in manufacturing processes may be classified as follows: **The Soft Mud or Soft Plastic Process**, where shapes are formed from clay or other raw material containing 15 per cent or more of water. Such mixtures have a soft consistency which allows them to be shaped by hand for only a little pressure is required to cause free flow within the material.

From the earliest times this process has been used for shaping bricks, tiles and many kinds of pottery and it is still used almost exclusively in the manufacture of earthenware, stoneware and porcelain. Its use for building bricks has greatly lessened during the last century because mechanical methods of shaping are much cheaper for bricks, tiles and various kinds of pipes. The shaping is effected in moulds of iron, brass, wood or plaster of Paris. For simple shapes a one-piece (or sometimes a two-piece) mould is used. It is filled with the soft paste which is either

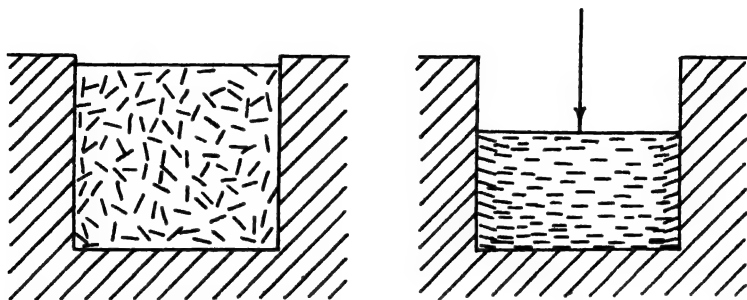


FIG. VIII.30.

THE ORIENTATION OF PLATEY PARTICLES IN PLASTIC MASSES AFTER PRESSING

pumped or pressed by the workers' thumbs and fingers so that all the corners are compactly filled. Any surplus clay is then removed by a taut wire. For more complex shapes each portion of a multiple piece mould is filled separately with the paste, then pieces are joined and fastened together and compacted as before. The moulds with their contents are either emptied at once or are set aside for their contents to stiffen and can then be turned out of the mould.

Soft-mud pastes are used in all jiggering processes and in the manufacture of flat-ware of all types.

Some building bricks and a few low-grade fireclay products are manufactured by this process, for elaborate mechanism is not required and consequently costs can be kept to a minimum. Soft-mud moulding is often employed when complex shapes are to be made; the mass readily flows under a small applied pressure until it completely fills the mould. One serious disadvantage of using mixtures of a high water content is that considerable shrinkage may occur on drying and the fired product has a comparatively open texture and low crushing strength.

Wire-cut bricks are normally prepared from clays with a moisture content between 13–18 per cent. The water is incorporated in a horizontal pug-mill and thoroughly blended with the clay. The plastic mass is then forced through an aperture, nozzle or die and emerges as a ribbon and can be cut into the required shapes by wires or thin blades. It is customary to de-air the clay in the pug or auger as this usually increases the wet strength and reduces laminations and surface-shear defects. Although de-airing is a vital necessity in the production of wire-cut bricks from Coal Measure clays, some of the Wealden clays extrude more satisfactorily if it is not employed.

Fully automatic processes have been introduced which can manufacture up to 3,500 bricks per hour. The nozzle can be so designed to produce perforated, hollow or tongued and grooved bricks, and rusticated or sand-faced shapes can be made with simple accessory equipment.

Salt-glazed pipes, quarry and tile-bats are also largely extruded products using a plastic body.

The Stiff Plastic or Stiff Mud Process involves the use of materials with a water content of between 8–15 per cent, i.e. there is just sufficient moisture present or added to permit the material to flow under high pressure.

Many building and most fireclay refractory bricks are made in this way. The stiff plastic machine consists of a rotating table containing a series of moulds which are filled in turn by paste forced into them from a vertical pug mill and, after the table has made a partial rotation, the paste in the mould is subjected to pressure. After a further partial rotation of this table, the bricks or other articles are released from the mould and removed from the machine. They are then usually pressed a second time to improve their shape and finish. Most articles made by this process can be sent direct to the kiln without needing any time in a dryer, but for some shapes a partial drying is necessary.

The Semi-dry Process is used where the associated water is about 5–9 per cent. Many clays and shales occur in the natural state with a moisture content in this range and if they are soft in consistency they can be formed directly into bricks or other shapes without further treatment. This is particularly so with some building brick clays of which Oxford Clay is perhaps the best known.

Considerable pressure (up to 10,000 lb. per sq. in.) is required to produce the required shape from masses in the semi-dry state and in order to reduce lamination effects and produce a uniform density throughout, the pressure should be applied both from above and below.

Dry Press Methods are more commonly employed in the manufacture of non-plastic ceramic bodies. The moisture content is about 3–5 per cent and is just sufficient to permit the powdered body to hold together when tightly squeezed.

Although very great forming pressures are required (up to 100,000 lb. per sq. in. for special refractory shapes), the body so formed has an exceptionally high density and the drying and firing shrinkages are at a minimum because the void space or porosity is less than that in a body formed by other methods. Unless precautions are taken to remove entrapped air prior to or during the forming, pressure laminations may develop; they are caused by small pockets of air being compressed and then released during pressing—this is most serious when the individual grains are angular or platy.

There is always a tendency when clay and other masses are pressed, for some degree of particle orientation to occur and it is a frequent source of weakness and failure particularly in clay bodies, for in them laminations and shear fractures are easily developed. Such faults occur more frequently where the water content is sufficient to allow free flow and where the forming pressure is high; consequently bodies formed by the soft mud and stiff plastic methods are particularly liable to such faults.

A detailed study of the 'fabric' of a body which has been subjected to pressure

in various ways has been undertaken by Williamson¹ and also by Haefeli and Amberg.² Both groups of workers used a similar technique in which the test pieces were made of alternate layers of differently-coloured wet clay. The resulting masses were then subjected to pressure applied in several ways and the changes in the coloured pattern were observed. The stresses and laminations which are produced in an extruded bar of clay have been examined in detail by Williamson and his results are of the greatest value in explaining many of the defects which occur in clay masses. The flow properties of the plastic body cause typical particle orientation in certain well-defined directions; in addition the authors have been able to show that stress fractures occur in two planes mutually at right angles.

Such investigations into the 'fabric' of a clay body when subjected to forming pressures will undoubtedly lead to a more detailed appreciation of the many contributory factors involved in the shaping of plastic masses.

¹ Williamson, W. O., *Amer. J. Sci.*, 245, 645, 1947.

² Haefeli, R. and Amberg, G., *Schweiz. Ton.-Industr.*, Nos. 1-6, 1949.

CHAPTER IX

CHANGES IN THE PHYSICAL STATE OF CERAMIC MATERIALS BROUGHT ABOUT BY THE REMOVAL OF FREE WATER

THE clay minerals are mostly hydrated aluminosilicates and contain OH-groups which, when the clay is heated to a sufficiently high temperature, escape in the form of water vapour—known as combined water, constitutional water or crystal water. They also contain water in other forms—some being adsorbed and in a state of slight combination, whilst other water lies between the layers forming the mineral (inter-layer water or interstitial water); in most clays there is water occupying some or all of the open pores.

Water is usually added to all ceramic bodies to assist in the moulding of shapes. The amount used depends upon the material and the method of shaping and varies from around 5 per cent in dry pressing to 30 per cent and above (by weight) in slip casting. Such water is termed free water and its removal must be complete before the ware is fired, otherwise serious faults may arise.

The removal of water may be effected in various ways, of which the most important are:

- (a) *Evaporation* or *drying*—usually by the application of heat.
- (b) *Filtration*, more especially by means of filter-presses.
- (c) *Absorption*—as in plaster moulds.
- (d) *Sedimentation* or *Settlement*.
- (e) *Centrifuging*.
- (f) *Electro-osmosis*.

The *complete* removal of water can be effected only by the first of these methods; the others produce a paste which may contain 10 per cent or more water.

The term *dewatering* is commonly used for describing the removal of large quantities of water from slips, etc., the term *drying* being usually restricted to the removal of water from pastes and solids; both terms are used rather loosely.

The term *dehydration* is being increasingly used for the removal of water particularly when the precise means by which the water is removed is not stated; this term includes the removal of water by means other than drying by heat though that is the most widely used method of dehydration.

Drying is effected by (a) exposing the material to a quantity of either cold or warm air which is sufficient to absorb and carry off the water, thus leaving the clay in a dry or almost a dry state; (b) heating the material so as to convert the water into steam, which then escapes into the atmosphere; or (c) by means of a dehydrating or desiccating agent, such as sulphuric acid, which absorbs moisture from the atmosphere surrounding the material to be dried.

The method which is most appropriate in any particular case must depend on

the nature of the material or article to be dried and upon the state of the water present. If a ceramic material consists of a slip or very soft paste it may be cheaper to effect a partial separation of the water by means of a centrifuge or a filter press and to complete the separation by drying the product.

At atmospheric pressure the drying is seldom complete at a temperature below 110°C. , but it may be effected at a much lower temperature *in vacuo*. Most ceramic articles are not dried completely but retain about 5 per cent of moisture when removed from the dryers.

Moist clay has a high vapour pressure as a result of the large surface area exposed for evaporation, but at ordinary temperatures the removal of water is so slow that, for commercial purposes, some form of heat must generally be used.

Furthermore, the process of drying is greatly accelerated if the moist air surrounding the material is progressively removed, because the rate of evaporation depends largely on the humidity of the surrounding atmosphere. Should the air be near saturation point with water vapour, the evaporation rate from the wet body will be drastically reduced.

Drying by Absorption is chiefly used when only a portion of the water is to be removed. It is due to the property of slabs or moulds of porous earthenware or plaster of Paris withdrawing water from a clay-paste or slip by capillary attraction. Any water which is not removed by this means may be removed by heating. The rate of drying can be greatly increased if the moulds and their contents are kept in a warm atmosphere.

Drying by Filtration is effected chiefly in filter-presses which consist of bags enclosed by plates in a frame. The bags are filled with slip, pumped in under pressure, and as the water flows out through the apertures in the mesh of the bags, the clay or other solid matter forms a cake which is solid enough to be handled though it is by no means dry.

Partial Drying by Sedimentation, consists in allowing a suspension to settle and then decanting off the surplus water. The resulting deposits are usually very soft pastes or viscous fluids. When a slip or body-slip is found to contain an excess of water (i.e. when its weight per pint is too low) it is allowed to settle overnight and a suitable quantity of clear water is then drawn off and the slip (if necessary adjusted by adding a little more water) is thoroughly mixed by blunging before being used.

Partial Drying by Centrifuge needs no detailed description. The material (usually a suspension in water) is passed into a centrifuge which drives the solid matter to the sides of the machine; the greater part of the water remains near the centre of the machine and can be allowed to flow out whilst the machine is running.

Drying by Electro-osmosis is seldom used on a commercial scale as it does not dry the material completely and is too expensive (see p. 500).

REMOVAL OF WATER FROM SLIPS

In a slip, the water usually constitutes the bulk of the material, the particles of solid matter being suspended in it. When such a slip is placed in a porous vessel, such as a plaster mould or the bag of a filter press, the greater part of the water passes through the pores of the vessel and so is separated from solid particles, most of which are too

large to enter the pores. If an extremely fine suspension (such as a colloidal sol) is treated in this manner, the particles may be small enough to pass through the pores, and consequently no separation of them from the water will be effected. The removal of water from a slip in the manner indicated is clearly a mode of filtration, the small particles of water passing through the pores of a filter which are too small to permit the passage of the solid suspended particles.

When a slip is allowed to remain quiescent for a sufficient time, many of the suspended particles will settle and some of the clear water may then be run off, or decanted and so separated. The same effect may be produced far more rapidly in a centrifuge which has several hundred times the force of gravity.

The whole of the water in a slip may also be removed by the application of heat, which converts the water into steam, but this method is usually too costly to be applied to slips without subjecting them first to one of the other methods mentioned in order to reduce the amount of water present.

REMOVAL OF WATER FROM PASTES

In a paste the water may be present in one or more of three forms:

- (a) A superficial film surrounding each solid particle;
- (b) As interstitial water, i.e. as water occupying the pores or interstices between the solid particles so that each solid grain is separated from every other by a superficial film of water and by the interstitial water;
- (c) The water may be absorbed into the colloidal material coating the grains, causing the colloidal matter to swell like soaked glue and each solid particle to be separated from every other by the colloidal gel.

Berridge¹ has calculated that if the volume per unit mass of a saturated clay ($\epsilon = 2.70$) is three times that of the same clay at maximum density ($\epsilon = 0.46$), when dry, the distance apart of the particles in saturated clay is $\sqrt[3]{2.7}$ or 1.39 times that in the clay at maximum density.

As long as sufficient water is present, the clay remains in a swollen state, but as it dries the particles are drawn closer together and the mass shrinks or contracts.

Only the interstitial water can be removed from a paste by mechanical means such as by subjecting the mass to great pressure, and even then the removal is incomplete, so that the only effective method of removing water from a paste is by some mode of drying. When the water is gradually withdrawn from a paste in this manner, each form in which it occurs is the cause of certain physical changes in the material, and the drying therefore appears to occur in several distinct stages, though these overlap to some extent.

The Mechanism of Drying. During the early stages of drying, evaporation from the surface of a clay body occurs at almost exactly the same rate as from a water surface (e.g. a pond) and continues at that rate until there is an insufficient supply of water from the interior of the mass.

The physical state of fine-grained material when a sufficiently large amount of water is present may be imagined to be as shown in Fig. IX.1a. Each particle is

¹ Berridge, B., *Engineering*, 131, 128, 1931.

separated from its immediate neighbours by a water film of a relatively appreciable thickness. In this state, the clay or ceramic body can be easily moulded because the 'free water' surrounding all particles acts as a cushion and permits the mass to flow, either unaided or under slight pressure.

The water film is a *continuum* throughout the mass and hence the water surface exposed to the atmosphere is unbroken and evaporation can proceed at a rate similar to that from a volume of water with the same surface area.¹

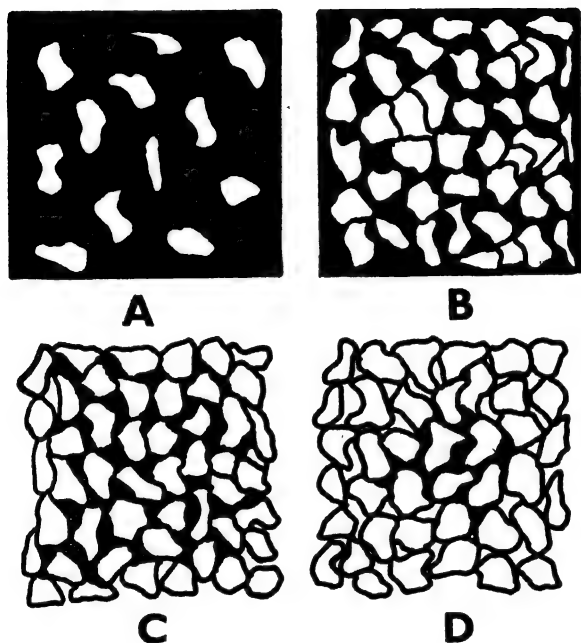


FIG. IX.1. STAGES IN THE DRYING OF A PLASTIC CLAY BODY

(A) The initial state with excess, free water; (B) particles just touching each other—the critical point; (C) the destruction of the continuous surface-water film—water can evaporate only from the ends of capillaries; (D) the final stage of water contained only in isolated pockets in the dried mass

As water is lost by surface evaporation, the continuum in the mass is preserved by a drawing together of the particles and an over-all *shrinkage* occurs. The clay mass will lose water as though there were a free, surrounding water surface until the solid particles touch each other and the water within the mass can no longer maintain a continuous film (Fig. IX.1B).

In this initial stage of water-loss, the rate of drying, if conditions are kept uniform, is constant throughout. The rate of shrinkage of the mass also very closely

¹ Macey, H. H., *Trans. Brit. Ceram. Soc.*, 37, 131, 1937.

Sherwood, T. K. and Comings, E. W., *Ind. Eng. Chem.*, 25, 311, 1933.

parallels the rate of loss of water and is constant in the region. For these reasons, this first period of drying is known as the *constant rate period of drying*.

The rate of drying in this period depends on that at which the water leaves the surface of the article and is absorbed and carried away by the air in the dryer. If this air is completely saturated (i.e. its humidity is 100 per cent) there will be no drying at all. If the air is stationary, drying will continue until the air is saturated and will then cease. Only if the air is removed, either mechanically or naturally, will drying occur and the rate of drying will depend chiefly on that movement. The hotter the air, the more water will it hold and the more rapidly will it dry the goods, so long as it is not fully saturated, but air which is too hot and too dry may cause cracking.

The water removed from the articles in this state is sometimes termed the *shrinkage water* and the amount of water remaining in the body at the end of this stage is termed the *critical moisture content*.

At the end of the first stage, the articles will then be in a *leather-hard* or *black-hard* state and will contain about 7–10 per cent of water (based on the fully-dried weight).

In the *second stage of drying*, which commences when the solid particles in the mass are in contact with one another, a capillary system is formed. The surface of the mass can no longer behave as a continuously evaporating film, because the water will be drawn into the pores between the solid particles of material.

Precisely what occurs during the removal of the remaining water has not yet been fully established. Morgan and Hursh¹ consider that the process is mainly one of vapour-diffusion to the surface from the ends of the narrow capillaries of water. Ceaglske and Hougen² suggest that water is drawn through the capillary system by surface tension forces and evaporated from the surface. Macey,³ on the basis of his studies on the transmission rate of liquids through porous solids, has advanced the theory that water is removed as a result of the rise in external pressure caused by the repulsion of particle surfaces which are in close proximity. The rate of evaporation depends only on the number of exposed ends of narrow columns of liquid in the mass (see Fig. IX.1c) and as these will become progressively less in size and smaller in number the rate of water loss will fall. Eventually only small isolated pockets of moisture will remain which are so completely enclosed that the rate of evaporation will fall almost to zero (Fig. IX.1d).

This final stage in the drying is known as the *falling rate period* and in many bodies the change-over in drying mechanism is so well defined that the *critical point* can be accurately established (see Fig. IX.2).

The drying behaviour of all ceramic bodies which are agglomerations of small particles follows the same general pattern although the ultimate rates in the two periods and the position of the critical point depend upon many factors.

The Shrinkage on Drying. Fig. IX.3 shows the linear shrinkage as a function of water content for three typical materials, a highly plastic clay (A), a feebly plastic kaolin (B) and a non-plastic sand-aggregate (C).

¹ Morgan, W. R. and Hursh, R. K., *J. Amer. Ceram. Soc.*, **22**, 271, 1939.

² Ceaglske, N. H. and Hougen, O. H., *Ind. Eng. Chem.*, **29**, 805, 1937.

³ Macey, H. H., *Trans. Brit. Ceram. Soc.*, **41**, 73, 1942.

In all ceramic materials where the moisture content is high, the initial rate of shrinkage on drying is virtually constant. The position of the critical point (i.e. the water content at which free surface evaporation is no longer possible), varies from about 20 per cent in a plastic clay to 4 per cent in a non-plastic sand. The change-over point is more clearly defined in the latter material; in clays there is sometimes

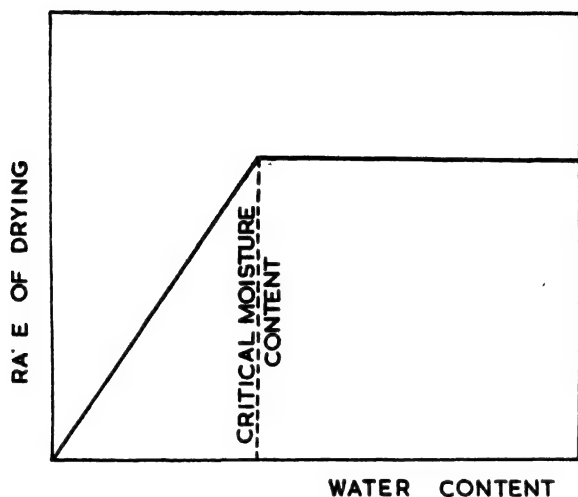


FIG. IX.2. THE RATE OF DRYING IN CERAMIC BODIES

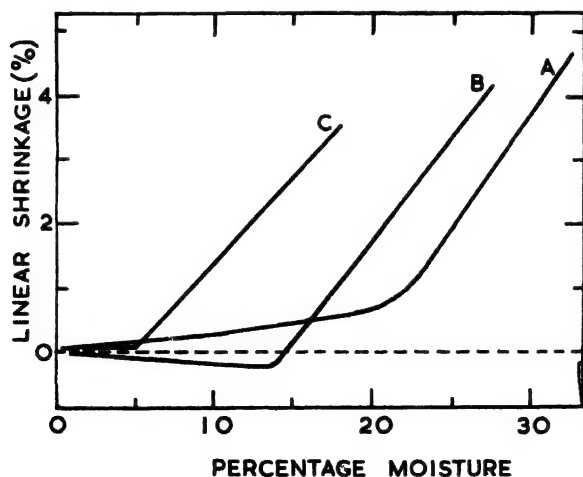


FIG. IX.3. THE RELATION BETWEEN THE SHRINKAGE AND THE WATER CONTENT DURING THE DRYING OF CERAMIC MASSES

(A) A plastic clay; (B) china clay; (C) a sandy clay

no well-marked transition and appreciable shrinkage occurs at a water content below the critical value.

Clays are composed of inherently fine-grained particles which would be expected to have a fine capillary pore-system, hence the amount of retained water will be greater than in sand where the particles are larger and more rounded in shape. The shrinkage in clay bodies at water contents below the critical point has been attributed to a rearrangement of colloidal particles and to the loss of water contained within the structure of certain minerals. The amount of shrinkage below the critical point is, however, relatively small compared with the amount in the constant period of drying.

Plastic clays and clays rich in colloidal particles shrink more than 'lean' ones, but there is no definite relation between the plasticity and contraction of a clay, as the latter property is dependent on several factors other than the plasticity of the mass.

The fact that clays lose water in two stages is of the greatest importance in drying practice. Because shrinkage is so great in the first stage and virtually non-existent in the second, stresses may develop which give rise to drying cracks and warping. This may be clearly demonstrated by considering the conditions in a slab of moist solid being dried by evaporation from the two side faces as illustrated in Fig. IX.4.

Water is lost only from the exposed faces and hence a *moisture-gradient* is set up across the brick, as at the times t_1, t_2, t_3 in the diagram. The curvature in the gradient curve depends on the rate at which water is being removed and the slower the drying-rate the less will be the gradient.

As more water is lost, the moisture in all parts of the slab is reduced but at all times the percentage in the external areas of the two side-faces will be less than in the centre of the slab. Consequently a condition will exist, at some time, t_3 , when the outside portions of the slab will have a moisture content below the critical point, yet in the interior the amount of water may be much above this point. The outside layers will, eventually, become almost dry and it is only then that the moisture gradient will be reduced as water from the inside of the slab continues to evaporate.

The moisture gradient at any time in a cylinder being dried from one face can be predicted mathematically; the equation is similar to the one representing the temperature fall across a slab which has been heated to a certain temperature and allowed to cool with one face only exposed. The mathematical expression is

$$-\frac{dm}{d\theta} = k \frac{d^2m}{dx^2}$$

where m is the volume concentration of water; θ is the time interval, x is the distance from the cool face and k is a constant.

This equation has been applied by Gilliland and Sherwood¹ to interpret the condition in a slab of drying clay.

The shrinkage in a composite body which is being dried is great above the critical point, but is substantially reduced at low moisture contents. As long as all

¹ Gilliland, E. R. and Sherwood, T. K., *Ind. Eng. Chem.*, 25, 1134, 1933.

parts of the slab have a moisture content above the critical point, and, provided the rate of loss is uniform throughout, the shrinkage will be the same at all parts of the body. Once the external areas have dried, however, and contain less water than the critical point of the mass, no further appreciable shrinkage can take place, although the centre region continues to shrink.

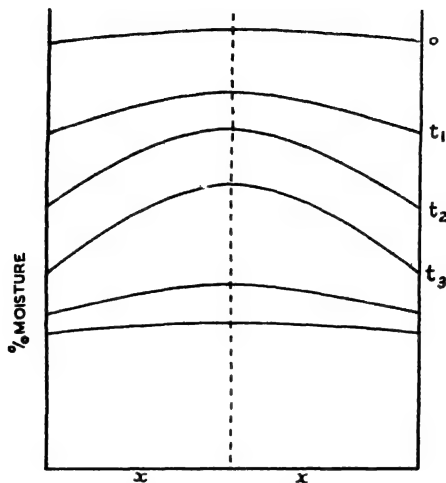


FIG. IX.4. THE MOISTURE GRADIENTS IN A SLAB OF MOIST CLAY BEING DRIED FROM THE TWO SIDE FACES

The critical point corresponds to the condition when the body becomes *leather hard* or *black hard* and, consequently, is less able to accommodate stresses. If the external parts of the drying slab are in this condition whilst internal areas are still shrinking considerably, there will be a tendency for faults and cracks to develop. Hence, whenever the moisture gradient across the block or article being dried is great, faults and cracks are liable to form and safe drying can only be accomplished either by (a) reducing the drying shrinkage, or (b) reducing the moisture gradient.

The Shrinkage may be reduced by:

(i) Making the articles from a stiffer paste. The amount of water to be lost before the critical point is reached is thereby reduced and hence also the shrinkage.

(ii) Using a higher proportion of non-plastic large-grained material in the raw material batch. Such additions have a dual beneficial action; they reduce the overall content of colloidal material and they also build up a rigid skeleton throughout the mass which reduces shrinkage and preserves an open structure which facilitates the drying. Sand and grog are frequently employed for this purpose.

(iii) Using clays and materials which are less colloidal in character, because although other factors are involved, bodies with a high proportion of colloidal matter shrink more than others. Thus pastes made wholly of ball clay may shrink more than 20 per cent when dried. China clays generally have a much smaller contraction and,

when added to a ball clay, will reduce the drying shrinkage of the latter. Flint, felspar and similar materials have a very low shrinkage.

(iv) Adding a suitable electrolyte to the paste. The mechanism whereby ions of different kinds influence the drying shrinkage is not yet fully understood, although it has been the subject of considerable research in recent years. Under different conditions, the same electrolyte addition appears to produce varying effects and it may be that several underlying causes are involved.

A flocculated clay is dispersed by small amounts of electrolyte and hence a larger proportion of solid material can be contained in the paste; this will reduce the drying shrinkage. On the other hand, too much electrolyte may give rise to thixotropic conditions with a consequent large drying shrinkage. The individual absorbed ions in a clay also have a marked influence on the shrinkage; calcium bentonite, for example, has a much smaller drying contraction than the sodium variety and this may, in part at least, be attributed to the hydration of the cations themselves.

When mixed with the same amount of water a flocculated clay can be dried far more quickly and shrinks to a smaller extent than a deflocculated specimen. The agglomerated mass is more open in texture and permits the freer removal of water to the surface. Fewer drying defects are encountered with flocculated clays but such bodies have a lower strength than those prepared from a deflocculated mass.

Chlorides, sulphates, and some acids are frequently added to clays to flocculate them and facilitate drying. The amounts added must be small and they should be rigidly controlled otherwise deleterious effects will be introduced.

The moisture gradient across a drying slab may be reduced by:

(i) Slowing down the drying rate by carefully controlled hydrometric conditions. Water contained in the centre portions of a slab will be transferred to the surface at a rate depending principally on capillary and surface tension forces. If the permeability of the mass is low the diffusion of moisture in this way is bound to be slow. If the rate of surface evaporation is reduced, the diffusion process will more nearly equate the moisture gradients.

(ii) Increasing the permeability of the mass. If many of the pores in the material are large, water can readily escape, but where the pores are minute, liquid or vapour transference is not easy. Thus, a lean clay, such as china clay may safely be dried more rapidly than a highly plastic clay, although both contain the same initial amount of water, because the former is more permeable. Sand and similar coarse-textured material have an even greater permeability and are far less susceptible to severe moisture gradients.

(iii) Evaporating the water at a more uniform rate throughout the mass. The rate of evaporation depends upon the relative humidity of the surrounding atmosphere and also on the temperature to which the mass is heated. In a body which is at a constant temperature throughout, the external portions exposed to a drier atmosphere must lose water at a faster rate than the interior where the atmosphere will be more saturated, but, if the inside of a drying block can be raised to a higher temperature than the outside, the rate of internal evaporation can be increased and the moisture gradient reduced.

It is this principle which is utilised in tunnel and humidity dryers.

METHODS OF DRYING

Humidity Dryers. As it is obviously not feasible to raise the inside of a block to a higher temperature than the outside by a single operation, the whole article must first be heated to a uniform temperature and then the outside cooled to achieve the desired results for humidity drying. It is of the utmost importance to ensure that no water is lost during the initial heating otherwise differential shrinkage is bound to occur. Consequently the surrounding atmosphere during the heating process has to be kept fully saturated with water vapour, and reduced in humidity only after the desired temperature has been attained.

Tunnel dryers usually operate on the so-called counter-flow principle as illustrated in Fig. IX.5.

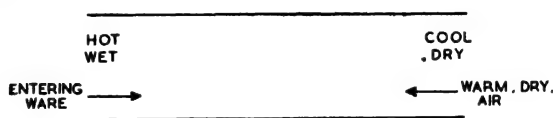


FIG. IX.5. DIAGRAMMATIC REPRESENTATION OF A TUNNEL DRYER

The ware to be dried is loaded on cars which move slowly through a tunnel usually about 100 ft. long. Warm air, which may be drawn from the cooling kilns, enters at the opposite end and during its passage down the tunnel becomes saturated in moisture derived from the ware which has proceeded some distance into the tunnel. The most efficient humidity dryers incorporate a heating unit near to the ware entrance, hence the wet articles encounter an immediate hot, saturated atmosphere. No water is lost initially, but the temperature is raised throughout the complete body.

As the ware proceeds along the tunnel, the surrounding atmosphere becomes progressively cooler and drier, thereby reducing the outer parts of the ware in temperature and permitting evaporation. The interior of the ware remains at a higher temperature and if the rate of passage of the cars through the dryer is carefully controlled, the moisture gradient across the body may be kept down to a minimum.

Finally, the loaded cars pass out at one end of the dryer, with their contents practically dry, whilst the warm air saturated with moisture, passes out through a chimney at the other end of the dryer.

Many of the tunnel dryers used in the clay industries operate under somewhat different conditions. They make use of waste heat from kilns and it is customary to feed this through the tunnel dryer in the opposite direction to the ware. Consequently the ware, in its transit through the dryer, encounters increasingly warmer and drier air. Despite this fact, if conditions are carefully controlled, entering ware is surrounded by saturated air and can be dried uniformly. It is important, however, to secure a correct balance between the temperature and velocity of warm air and the rate of passage of ware through the tunnel dryer.

A similar method, but taking the air through a series of loaded *chambers*, the goods to be dried remaining stationary, also gives very satisfactory results. Such dryers are known as *Keller* or *chamber* dryers.

Humidity driers have not only reduced the losses in the drying process but also considerably improved the space and time factors.

Hot Floor Dryers. Before humidity dryers were introduced, it was customary to dry all the ware after forming, on *hot floors* or *shelves* heated by steam or by waste gases from the kilns. In this way, water was evaporated entirely from the surface layers exposed to the atmosphere in the dryers, thereby creating large moisture gradients throughout the ware. Excessive losses through differential shrinkage could be avoided only by very slow drying entailing an operation of many days. In corridor and tunnel dryers, the operation is completed in a few hours.

Macey¹ has compared the relative advantages and disadvantages of hot floor, tunnel and chamber dryers and the thermal efficiencies of several modifications of each type. He concludes that whilst tunnel and chamber dryers are of comparable thermal efficiency, hot floor methods can never be more than half as efficient. Other factors must be considered and the capital cost and the necessity for skilled operation offset some of the advantages of tunnel and chamber dryers.

Hot floor drying is still in common use in this country in the manufacture of building bricks and articles of special shape such as architectural terra cotta and large refractory blocks. It is being superseded in most sections of the industry by controlled humidity and other methods of drying.

In some porcelain and earthenware factories, the ware is dried in the moulds in a few minutes, the moulds resting on tubular metal shelves which convey hot air to small jets above each mould.² The control of temperature and humidity of the air is very important and only thin ware can be dried in this way.

Alternative Methods of Drying. In recent years, other methods of drying ceramic ware to eliminate differential shrinkage have been suggested. They also rely for their efficiency on the rate of evaporation from the interior being comparable to that from surface layers.

Jefremow³ has claimed that small articles can be efficiently dried by passing an *electric current* through the mass. The internal resistance raises the temperature of the block and evaporation is uniform throughout. The method is of value for small specimens and as the moisture content falls, the drying rate is progressively reduced owing to decreasing conductivity.

Infra-red drying of ceramic ware has received considerable attention particularly in America. Heat rays of longer wavelength than the visible spectrum are readily adsorbed by water although they are transmitted by the surrounding air; consequently, the ware is heated although the atmosphere remains cool. The efficiency of infra-red methods for ceramic materials is still a matter for conjecture especially when large-sized objects are to be dried.

In *dielectric* or *high frequency* heating, as in infra-red drying, the ware is exposed to the radiation of a particular wavelength but high frequency radio waves are employed. These induce electrical effects in the wet ware which heat up the body. Several investigators⁴ claim that the method is valuable even for complicated large-sized clay shapes, although large scale units are not used extensively.

¹ Macey, H. H., *Drying in the Heavy Clay Industry* (H.M.S.O., London, 1950).

² Hancock, W., *Ceramics*, 5, 408, 1953.

³ Jefremow, G. L., *Ogneupory*, 1, S, 33, 1936.

⁴ Vassiliou, B. and White, J., *Trans. Brit. Ceram. Soc.*, 52, 377, 1953.

All methods of drying used on the industrial scale aim at reducing the water content below the critical point. This ensures that further excessive shrinkage will not take place during the initial stages of kiln firing, hence there is no necessity to waste time and fuel in more thorough drying. In heavily-grogged articles and in others in which the proportion of non-plastic material is high, it may be necessary to reduce the water content below 5 per cent, but, in other cases, appreciably more may be present.

That this statement should not be applied generally is well known to all who have had experience of the firing of clayware by rapid cycle methods. In the early stages of firing the fast rate of temperature rise induces a high temperature gradient across articles particularly those of large dimensions. Small quantities of entrapped water in such bodies are driven into the cooler interior and there may accumulate. When the water finally volatilises it may do so with disruptive violence and either shatter completely the block in which it was contained or cause flaking or blistering of the outside layers.

Extruded articles and those made from finely divided clays are particularly prone to this type of fault which may occur even though the body had been dried to a moisture content well below the critical point.

The 'blowing' of articles in this way can be eliminated either by ensuring that a maximum of 1 per cent water is present when articles enter the kiln, or by so adjusting the pre-heating of the kiln that adequate time at a comparatively low temperature (below 200° C.) is available for the complete removal of water.

PROPERTIES OF DRIED ARTICLES

Dry Strength and Hardness. When ceramic bodies are dried the strength of the article usually increases considerably. Clay ware shows a pronounced increase, common brick clays and many fireclays are hard enough to withstand considerable mechanical handling after the drying process.

The underlying mechanism of dry strength is still a perplexing, unsolved problem although several interesting theories have been advanced. It is well established that the specific surface area of the particles in a dried mass is directly related to the strength developed. Furthermore, it is known that the last traces of water adsorbed by a clay are intimately held and are driven off only with difficulty even at high temperatures. One explanation for the dry strength of clay bodies is based on this latter fact. The retained water is regarded as forming a thin film covering the surface of all particles and having a structure induced within it. When the particles are touching, such films may blend together thereby forming a *continuum* which extends throughout the mass; the more points of contact of particles, the greater will be the strength in the mass.

Another theory has been suggested by Weyl, which is based on the distortion of ions in the surface layers of particles. A simplified picture of the ions in a crystal is shown in Fig. VIII.1 (p. 418). A cation which is situated at some distance from the external layers is in equilibrium and balanced by evenly-spaced charges of opposite sign, but, a cation in the surface of the same crystal does not have a full quota of opposite, balancing charges surrounding it, hence there must be some distortion.

Weyl suggests that the ions in the surface layers are not at the normal separation distance and that this contraction may extend over several ionic layers in the immediate vicinity of the surface.

This concept of surface distortion is most valuable and some aspects of the unusual behaviour of small particles can be more fully understood on the basis of the irregular properties of the surface (see p. 430). By assuming that such distortion exists, a mechanism which accounts for the dry strength of agglomerated masses can be advanced.

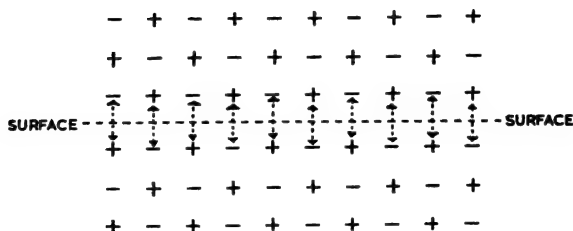


FIG. IX.6. A SUGGESTED MECHANISM FOR THE BONDING BETWEEN TWO ADJACENT CONTACT SURFACES

Because ions in the surface layers are unbalanced electrically, they will have a natural potential for attracting other ions, which will be rigidly held by electrical bonding. If another surface, also with distorted external groupings makes contact with the former the two adjacent surfaces can share their unbalanced electrical fields as illustrated in Fig. IX.6. The forces between such particles will be partially ionic in character and considerable pressure will be required to force them apart. The greater the surface areas in contact the higher will be the strength of the aggregated mass. Therefore, clays and similar materials in which the particles are, for the most part, small and plate-shaped are expected to have large dry strengths.

Although clay bodies are usually stronger after drying, their elasticity decreases and they become more brittle. As long as a small amount of water is present in a clay mass, flow is possible so that the body is able to 'give' and thereby accommodate stresses; but, in a completely dry body, the bonding is rigid and there is virtually no deformation before fracture takes place. For this reason, articles are better cut and drilled or otherwise shaped when they are in the 'green' state than when they are dry.

Hygroscopicity is a term applied to dry materials which absorb water when exposed to moist air. Clays which have been thoroughly dried possess this property but the proportion of water so absorbed is usually very small and never sufficient to make the mass fully plastic. Montmorillonite-type clays can reabsorb up to 15 per cent of water under ordinary conditions of humidity and in doing so undergo considerable expansion.

DEFECTS DUE TO INCORRECT DRYING PRACTICE

UNDOUBTEDLY many defects in ceramic articles can be attributed to incorrect methods of drying. The faults, in some cases, are not apparent until the ware has

been fired, when they have been accentuated by changes brought about by the heat treatment.

In general, the defects which arise as the result of bad drying methods are of two types: (a) those due to differential shrinkage and the consequent induced stresses in the ware; and (b) those due to the migration of the finer particles of the body by moisture transference to the drying surface.

The most obvious effect of *differential shrinkage* on drying is the *cracking* of ware. This may take many forms but it is most usual for the faults to appear parallel to a face, which is drying more rapidly than other parts of the body. Whilst the material has a water content above the critical point, all parts of the body are plastic and should one area shrink more rapidly than others the strain can be accommodated. Once the leather-hard condition has been reached in part of the ware, deformation is less easy and areas with a high moisture content tend to shrink away from those which are drier. Cracks develop along inherent lines of weakness which in pressed ware are at right angles to the direction at which pressure is applied. Bricks tend to show lamination cracks running parallel to their large face; extruded blocks occasionally show S-shaped cracks along lines of weakness induced by helical movement of the body during forming.

In bodies of irregular shape, the thinnest sections dry more readily and cracks appear at the junction with thicker parts of the ware.

Moulded or cast bodies, especially hollow-ware articles may crack at mould junctions during drying, where there is a line of weakness caused by irregular particle arrangement.

Another defect in ware which is associated with uneven shrinkage is *warpage* or *deformation*. This is most common in thin-ware, but it is also found in large bodies where movement during drying has been restricted by contact with a floor or shelving. Warpage is caused by stresses which arise from uneven drying shrinkage in the body, but where the elastic or plastic nature of the material has permitted movement without cracks developing.

Many faults, normally attributed to incorrect firing, may have their origin in incorrect drying practice. *Dunting* in glazed ware is often due to hair-cracks which have developed at the edges of the body during drying. This is a not too uncommon phenomenon in glazed terra cotta which has been dried on hot floors. The dunting in such cases is limited to one edge or face which has been dried too rapidly.

Shelling may also be caused by improper drying of ware after the application of the glaze slip. Such faults are easily remedied by the correct control of the consistency of the glaze slip, but the defect is apparent after drying and should be clearly differentiated from true shilling, which is due to the incorrect balance between the thermal expansion of the glaze and body and is apparent only after firing.

When drying involves the migration of water from the interior of the article to the surface, fine-particled material may also be transported and deposited in the surface layers. This leads to *skin-formation* and an alteration in physical and sometimes chemical properties of the outside layers relative to the internal areas.

Because of the difference in body composition in various parts of the ware as a result of migration, *cracks* and *warpage* are liable to develop on firing, and frequently surface layers peel off during kiln firing.

The skin formation may be so serious that an impervious layer forms which retards further drying. In such cases, the article is liable to *disrupt* during kiln firing due to the vaporisation of the uneliminated water. An impervious skin formed during drying increases the tendency to '*black-heart*' formation by restricting the free access of oxygen during the cleaning period.

Soluble salts which may be present in the body are readily transported to the surface layers during drying and if they are large in amount they can produce serious *discoloration*. The surface of red-burning ware is frequently unpleasantly discoloured by calcium salts which have been transported during drying and produce yellow or buff areas on firing. Much of the *scumming* on bricks and other ware has a similar origin, but does not show up until the articles have been fired.

Provided that the defects which occur are clearly recognised and their cause ascertained, they can usually be eliminated by correcting the drying procedure. In theory, an efficient, well-regulated humidity dryer can dry all types of ware without inducing differential shrinkage or the transportation of fine particles. Many drying faults, however, are brought about by the incorrect use of such methods or by the failure on the part of the operator to recognise the principles involved.

CHAPTER X

THE EQUILIBRIUM STATE AND PHYSICO-CHEMICAL REACTIONS

It is generally recognised that, unless it is disturbed, a body remains at rest or, if it is moving, it will eventually come to a state of rest. Similarly, the normal state of a substance or mixture of two or more substances is to come to and remain at rest, i.e. to a state of equilibrium, until the conditions or circumstances are changed. These changes are of several different kinds and their effects are correspondingly different. A substance or mixture may be changed into another form or state without any change in its composition (*physical change*) or it may be converted into two or more different substances, one or more of which may escape as a gas (*chemical change*). When the cause of these changes has ceased to act, a new state of equilibrium may be reached.

Changes from one state of equilibrium to another are known as *reactions*, a word which is sometimes used with different meanings by chemists, physicists and engineers. Thus, chemists refer to reactions as:

1. Changes due to the action of one substance on another.
2. Changes due to the effect of a *force*, such as pressure, electricity, etc.
3. Changes due to the action of heat on one or more substances; heat being, for this purpose, regarded as a form of force.

Physicists and engineers often use the word *reaction* as the opposite of *action*.

The results of such changes are of two kinds:

(a) **Physical reactions**, in which there is no chemical change, but the substance may be changed from a solid to a liquid or gas (or *vice versa*) or into crystals of a different habit, as quartz into cristobalite or tridymite. Physical changes are produced by such processes as melting or fusing, solidifying, volatilisation or vaporisation, sublimation, solution, flocculation or precipitation and inversions and conversions.

(b) **Chemical reactions** in which one or more new products of different composition from the original substance are formed, as when copper is heated in air and is converted from a piece of bright metal into a mass of black copper oxide, or when carbon is heated in air and is converted from a black solid into a gas (carbon dioxide), or when a current of electricity is passed through water and converts it into two gases—hydrogen and oxygen.

There is frequently no sharp distinction between chemical and physical reactions in practice—though theoretically they are quite distinct—because a physical change such as a great reduction in the size of the particles, may bring about a chemical reaction at a much lower temperature. A molten mass may have the same composition as the crystals which form on cooling it (physical change), but many molten ceramic materials are not pure, and the crystals may have a composition different from the original liquid and still more different from any of the liquid which

forms a slag or glass when cold; the latter case may be regarded as a chemical change on crystallisation or as a physical separation of crystals of one composition from a liquid of another composition.

In consequence of this ambiguity, it is usual to refer to many of these changes as the result of *physico-chemical reactions*, without making any closer distinction between them and to regard such reactions as causing the initial substances to form products of a different type.

Associated with such changes are energy effects which are usually manifested as heat. Thus some reactions take place with the liberation of heat and are termed *exothermic*, whilst others need to absorb heat from their surroundings and are therefore referred to as *endothermic*. The energy change may not be developed solely as heat; for example, atomic transformations are manifested by light, heat and explosive forces. It is more correct therefore to regard a reaction as a system where the initial energy state is different from the final one. Physical chemists refer to the energy factor as a change in *entropy*.

Physical Changes. Physical changes in the state of a substance or mixture are usually due to the effects of pressure or heat and, more rarely, to the effect of light, magnetism, electricity and other physical forces.

They are chiefly concerned with:

1. Changes in form, e.g. from solid to liquid or to gas or *vice versa* without any decomposition.
2. Changes in volume, e.g. expansion, contraction (shrinkage), which may lead to changes in texture, hardness, porosity, density and crystalline form.
3. Changes in other physical properties such as viscosity, plasticity, 'strength', and optical and electrical properties.

Some of these apparently physical changes, especially when caused by heat, may be affected by chemical changes which accompany them, such as the reactions which occur when, as the result of heating, some portions of a solid mixture begin to fuse and the resulting liquid then reacts with some of the remaining solid and forms new chemical products instead of acting merely as a solvent. For this reason, readers should refer to Chapters XI and XII which deal with the effect of heat on ceramic materials as well as to page 647 in the present Chapter.

Chemical Reactions. The chief difference between chemical and physical reactions is that the product of a chemical reaction is of a different composition from that of the original material, so that chemical changes appear to be due to forces of a different nature though some physical forces may also be involved.

The most characteristic force associated with chemical reactions is that known as *chemical affinity*—a term which is not very appropriate as *dissimilar* atoms attract one another rather than similar ones, but it is still so largely used that it must be retained.

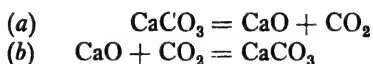
Modern chemists regard the force which produces chemical reactions as the tendency of each atom to surround itself with a balanced shell of electrons (see Chapter II) and in so doing, it effects the combination or rearrangement of atoms, ions and molecules of which the material is composed. In this sense, it is the unbalanced nature of any atomic grouping which largely determines its reactivity and the possibility and extent of any chemical reaction.

The extent to which various substances will react with one another also depends largely on their physical state (this, in turn, being related to their temperature); thus, liquids react more readily than solids, and gases more readily than liquids. In each case, this is partly a result of the freedom of the molecules and of their constituent atoms, the ultimate particles in a gas having the maximum mobility, whilst those in some solids have scarcely any freedom of movement, or any contact with other reacting molecules.

The ease and rapidity with which compounds react with one another also depend on their stability. A very stable substance in which the valencies or affinities of the various atoms for each other are well balanced will not be easily decomposed, but an unstable, unsaturated compound, or one in which the elements are only loosely united, will react readily.

All reactions, when once started, proceed until a state of equilibrium is reached. This state depends on a number of physical factors, such as temperature, pressure, surface tension, electric charges, etc. and if any one of these factors is changed the state of equilibrium will be destroyed and the reaction will proceed further either in its original direction or in the opposite direction. For example, when calcium carbonate (limestone) is heated to 1000°C . in a closed vessel, it is decomposed, forming lime and carbon dioxide gas. This decomposition continues until the pressure of the gas reaches a definite critical value. When the pressure reaches this value, the decomposition will cease, but will start again if a current of air is drawn through the vessel. By continuing to remove the carbon dioxide gas as fast as it is formed, the whole of the calcium carbonate may be decomposed. If, on the contrary, the lime so produced is subjected to the action of carbon dioxide, the original reaction will be reversed and calcium carbonate will be reformed.

The reaction and its reversal may be shown by two equations:

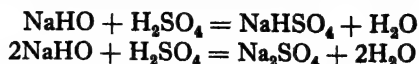


For convenience these may be combined, half arrows being substituted for the sign of equality:

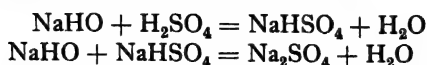


The most stable equilibrium which can be produced exists when two substances, each having a great affinity for each other, are combined together. Thus, silicon and oxygen when combined to form silica, produce an exceptionally stable compound, which is highly inert at temperatures below a red heat, though both its constituents (silicon and oxygen) are active elements.

Hence, when acids and bases react with each other, the final equilibrium product will be a substance (salt) in which both the reacting substances are present in maximum proportions. Intermediate states of equilibrium may occur when there is not sufficient of one material to combine with the whole of the other, and under such circumstances a basic salt may be formed if there is a deficiency of acid, and an acid salt if there is a deficiency of base. Thus, sodium hydroxide and sulphuric acid may react in two ways:

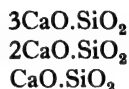


The second equation may also be written in two stages:



In the first stage (where there is a deficiency of base), the intermediate 'acid salt', NaHSO_4 , is produced, but is converted into the neutral salt on the addition of more soda.

Similarly, lime and silica can react with each other in various proportions, the product depending on the relative proportion of lime and silica present and on the temperature and other physical conditions. Typical products of the reaction of lime and silica are:



Chemical reactions always tend to form the most stable compounds possible under the prevailing conditions. Where several substances are present, those which have the greatest affinity for each other will react in proportion to their affinities until a state of equilibrium is reached. In the case of a single acid reacting with a single base, equilibrium (in this case neutrality) is reached when the maximum amount of neutral substance is formed.

Chemical reactions may occur between matter in the form of either solids, liquids, or gases. Thus, the following reactions are possible:

- 1. Reaction between two solids** is not common at ordinary temperatures and in most cases, if it occurs at all, it is so slow as to be negligible unless great pressure is applied, as when a mixed explosive is fired by a blow from a hammer. At high temperatures, many solids react with one another; thus lime and silica, when finely powdered and heated to about 600°C . combine to form calcium silicate, the action commencing before either of the substances is in a fluid state. As solid substances are so immobile, at least one of them must usually be in a very fine state of division and in close contact with the other before any combination can occur. The application of pressure, by bringing the particles closer together, facilitates the reaction.
- 2. Reactions between a solid and a liquid** are very common and may be exemplified by the corrosive action of acids and alkalies upon various solid substances and by that of fluid slags, etc., upon firebricks and other ceramic materials. The great mobility of the fluid brings the reacting substances into close contact and so facilitates the reaction. It should be noted that the fluid may be composed of one or more substances—either fused or in solution.
- 3. Reactions between a solid and a gas** are also common, especially in furnaces, as the gaseous products of combustion exert a chemical action upon the refractory linings as well as upon the contents of the furnace. In an oxidising atmosphere ferrous compounds are oxidised, whilst in a reducing atmosphere ferric compounds are reduced and deprived of some or all of their oxygen. Many changes which take place in metallurgical furnaces are due to reactions between solids and gases.

4. **Reactions between two liquids** are not of much importance in ceramic processes as the latter are chiefly concerned with solid materials.

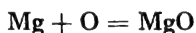
5. **Reactions between a liquid and a gas** are of minor importance in ceramic processes though they sometimes occur when molten materials are oxidised or reduced in furnaces or kilns.

6. **Reactions between two gases** often occur but do not concern the present subject as they do not directly affect any ceramic process.

TYPES OF CHEMICAL ACTION

THERE are five chief kinds of chemical action:

1. *Direct combination*, such as when magnesium and oxygen combine:

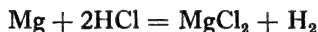


or when silica combines with lime:



This type of action is very common in ceramic processes, especially during the burning of goods. Other more complex reactions of the same type also take place, e.g. the combination of fluxes such as lime, soda, potash, magnesia, etc., with silica and alumina. These, together with reactions occurring during oxidation and reduction in ovens, kilns and furnaces, are considered in greater detail in Chapter XI.

2. *Displacement by an element or group of elements*; as when magnesium is attacked by hydrochloric acid:

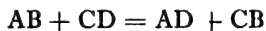


Reactions involving displacement are not very common in ceramic processes, but are largely used in some metallurgical operations.

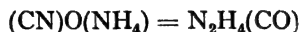
3. *Mutual exchange or double decomposition*, as when calcium sulphate and sodium carbonate interact:



In all such reactions, the acid radicle or ion of one base leaves it and becomes combined with another base, the acid radicle or ion previously combined with the latter then combining with the first base. The general equation for all mutual exchanges of this character is:



4. *A rearrangement* is said to occur when the atoms in a compound are recombined in a different manner. The classical example of this is the conversion of ammonium cyanate into urea:

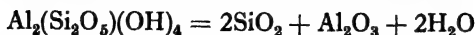


A modified form of 'rearrangement' probably occurs when alumina and other substances become polymerised on heating or when one form of silica such as quartz is converted into another, such as cristobalite, or *vice versa*.

5. *Dissociation* is said to occur when a substance is decomposed into its constituents, as when calcium carbonate is decomposed into lime and carbon dioxide:



or kaolinite is decomposed into free silica, alumina and water:



Many instances of dissociation occur in ceramic processes. Thus clay, bauxite, limestone, magnesite, dolomite, etc., are all dissociated when heated. Many of the impurities in ceramic materials are also dissociated by heat; thus, sulphides and sulphates are decomposed with the evolution of gas, limonite (ferric hydroxide) loses water and forms ferric oxide, and many hydroxides behave in a similar manner.

Although all chemical reactions can be included in one of the foregoing types, it frequently happens that several reactions succeed one another in such rapid succession that two or more types of reaction may be involved. The types just mentioned should, therefore, be regarded as guides and not as indicating a very marked dividing line between each type.

SOME FACTORS INFLUENCING CHEMICAL REACTIONS

THE factors which influence chemical reactions are very numerous and need to be carefully considered if the reactions are to be properly understood. The number of these factors, the difficulty in distinguishing completely the influence of each, and especially the fact that most ceramic reactions occur at high temperatures, are largely responsible for the small amount of definite knowledge concerning the reactions of clays and other ceramic materials. It is, therefore, very desirable to study each known factor fully, in order to determine its effect on the other factors and on the course of reaction, but the complexity of many ceramic reactions is so great that it is almost impossible, at present, to investigate them completely.

The principal factors which affect the course of chemical reactions between materials used in the ceramic industries are as follows:

- (a) Composition (chemical and mineralogical).
- (b) Sizes of particles and their distribution.
- (c) Temperature.
- (d) Time (duration).
- (e) Pressure.
- (f) Vapour pressure.
- (g) Atmosphere.
- (h) Surface phenomena.
- (i) Crystallographic structure and properties.
- (j) Viscosity.
- (k) Solubility.
- (l) Selective action.
- (m) Catalytic action.
- (n) Thermal conductivity.
- (o) Electricity.

- (p) Light.
- (q) Change of state (solution, fusion, volatilisation).
- (r) Intimacy of association.
- (s) Relative quantity of each substance present.

The *composition* of many ceramic materials has been described in Chapter V. The affinity of materials for each other and their tendency to react is described in greater detail in subsequent chapters.

The *size of particles* and their distribution may be a principal determinant of their reactivity. Reaction between two materials commences at their points of contact and many other reactions commence at surfaces of crystals. These factors are described more fully in Chapters XI and XII.

The *temperature* to which materials are heated influences the reactions which occur within them. Many substances which are stable under ordinary conditions react vigorously at elevated temperatures. Temperature is a principal consideration of the rate at which reactions proceed and of the nature of the equilibrium product.

In some cases, if a particular temperature is exceeded, the products of the reaction may take on a different character. The burning of bricks affords a good example, for in such cases too high a temperature will lead to the formation of an excessive amount of a liquid phase, which will reduce or even eliminate the combination and rearrangement reactions which proceed at a lower temperature. This point has to be closely studied particularly when firing clay bodies, and to secure a suitable product the 'working range' must be carefully established.

Time is almost as important as temperature in enabling a chemical reaction to take place. Although the combination of two single atoms may be instantaneous, yet when large numbers of atoms are involved, time must be allowed in order that they may come into contact with each other. Consequently, if the temperature attained is above the minimum required for the reactions to proceed, a sufficiently prolonged heating at that temperature will enable the reaction to progress to completion equally as well as it would do at a much higher temperature, only in the latter case a much shorter time would suffice.

It is a curious fact that no factor in the reactions of ceramic materials is less considered and less widely used than *time*. In the elementary books on chemistry and physics the experiments suggested are all selected for the speed at which they can be performed, so that most people with an elementary knowledge of chemistry and physics overlook the importance of the effect of time on all reactions particularly on those of a colloidal nature or on those which involve solid components.

The dispersion or flocculation of a reversible colloid often requires a considerable time and is rarely instantaneous. Hence tests or experiments of too short a duration are liable to be seriously misleading. This is clearly shown in the case of a fusible clay, or a mixture of clay with some fusible material such as calcium silicate. If the material is heated for only a short time, it will be necessary to raise the temperature very greatly before any signs of fusion can be recognised, whereas if the material be maintained sufficiently long at a much lower temperature, the same amount of fusion will occur.

When relatively large masses of material are concerned, the effect of time is

even more marked, because a heating of short duration will not alter the temperature of the interior of the mass and may render worthless, observations made upon physico-chemical changes in which sufficient time is not allowed to secure the necessary equilibrium or the ultimate state of the whole system.

This prolonged heating is known in the ceramic industries as 'soaking'. It is often much more costly than working the kiln at a higher temperature, but the latter would effect changes in the ware so rapidly that distortion and loss of shape would occur. By allowing the reactions to proceed more slowly (i.e. at a lower temperature), these risks are reduced and, in many cases, are wholly avoided. Where the shape of the product is not important, as in melting metal or glass or burning lime, it is usually desirable to work at as high a temperature as can be obtained without damaging the materials, as the reactions then proceed more rapidly and losses due to radiation, etc., are less serious.

A large part of the burner's skill consists in deciding what is the most suitable duration of heating as well as the maximum temperature to be attained. He has to adjust the temperature so as to complete the desired reactions as rapidly as possible, yet without undue risk of causing distortion of the ware by allowing the reactions to proceed too far.

The mistake, however, of trying to achieve by a short period of high temperature firing what is obtained only by long soaking at lower temperatures, must be carefully avoided; this is a serious fault of the test method known as Permanent Linear Contraction applied to assess the probable behaviour of refractory materials under long service conditions. In it, a sample of refractory material is heated for two hours at 1410°C . and conclusions are derived from the change in volume which occurs, as to the probable behaviour of that material when maintained for longer periods (perhaps several years) at considerably lower temperatures. It must be remembered that at higher temperatures reactions will occur which will never take place no matter how long the material is maintained at lower temperatures, so that the results of such tests are frequently invalidated and may often be misleading. Further details of this test method are described on page 728.

When the temperature of a kiln or furnace is rising slowly it is fairly easy to stop the heating at any desired point. If the temperature is rising rapidly considerable damage may be done after the heating has ceased because of the accumulated heat in the goods and in the structure.

Pressure usually accelerates chemical action, as it brings the reacting particles in closer contact with each other. In some cases (as where a firebrick is heated under a constant pressure until it collapses), the pressure does not greatly affect the reaction, but merely indicates the extent of the changes which have occurred.

An increase in pressure can, however, greatly accelerate chemical reactions in materials, particularly where water vapour is concerned. Clay minerals are known to rehydrate even though they have been heated to a temperature of about 800°C . The process may take several years to complete under ordinary conditions of water soaking but if steam is employed at high pressures, the reaction may be well advanced after a few hours' treatment.

J. H. L. Vogt¹ has shown that pressure has an important influence on the

¹ Vogt, J. H. L., *J. Geol.*, 30, 611, 1922.

formation of some complex silicates. He states that olivine, monoclinic pyroxene, feldspar, spinel, magnetite, etc., may be formed at either high or low pressure; melilite, however, is formed only under low pressure, and if the pressure is high, olivine or anorthite/bytownite is formed. Leucite occurs in rocks which have been subjected to only a low pressure, whilst microcline, biotite, and garnet occur when the rock during formation has been subjected to high pressure.

Pressure also has an important effect on the area of contact or intimacy of association of the particles. Thus, when shaping articles in a press or under pressure in a batting machine, less water is needed in the paste than when the same articles are shaped by hand.¹

Vapour pressure, which is the pressure at which the substance and its vapour are in equilibrium at a definite temperature, often exercises a great influence on the progress of a chemical reaction. The vapour pressure of liquids is much greater than that of solids; it increases rapidly as the temperature rises. When a substance which is decomposed on heating evolves a vapour or gas, which is unable to escape, the decomposition or dissociation continues until the vapour pressure of the gaseous product reaches a critical value. The decomposition then ceases no matter how long the heating is continued under the same conditions. If the temperature is raised, decomposition will commence and will continue until the pressure-equilibrium at that temperature is established. Thus, if limestone (calcium carbonate) is heated at 800° C. in an iron tube which has been exhausted of air, the stone will decompose until the vapour pressure of the carbon dioxide is equal to 85 mm. of mercury, and will then cease. On heating to 1040° C. further decomposition occurs until a vapour pressure equivalent of 520 mm. of mercury is reached.

On cooling, carbon dioxide will be reabsorbed and calcium carbonate reformed as the temperature drops until a vacuum is again established.

The changes in the vapour- or sublimation-pressure is expressed by the following equation:

$$\frac{dp}{dT} = \frac{pL_s}{RT^2}$$

where L_s is the molecular latent heat of decomposition, and the vapour formed has the volume RT/p at the temperature T .

The influence of the vapour pressure on the course of a reaction is very important in the lime-burning industry, for unless provision is made in a lime kiln to remove the carbon dioxide as it is formed, the limestone can never, for the reason just mentioned be completely converted into lime.

The vapour pressure of clays with different proportions of water varies with the clay and is thermodynamically related to the 'heat of wetting' (p. 426; see also Dehydration on p. 505).

The surrounding *atmosphere* often has an important influence and in some cases the form and rate of a reaction can be modified by changing the atmosphere.

In those reactions which involve oxidation, such as the burning of carbonaceous matter or the conversion of ferrous salts to ferric components, an excess of oxygen in the atmosphere is necessary, otherwise the reaction will proceed only partially or

¹ Mellor, J. W., *Trans. Eng. Ceram. Soc.*, 30, 235, 1931.

not at all if the atmosphere is reducing. Quite often the products of combustion are sufficient to retard or prevent further reaction because they surround the reacting material and prevent the free access of oxygen; for this reason, an adequate circulation of air during the cleaning period (300–750° C.) of the kiln firing of clay ware is vitally important.

The progress of many other reactions can be influenced by the nature of the surrounding atmosphere. This applies more particularly to those reactions in which a gas is evolved. The temperature and rate of decomposition of calcium and magnesium carbonates are greatly influenced by the amount of carbon dioxide in the air which surrounds them.

It is only in recent years that the influence on certain reactions of small amounts of gases either in the surrounding atmosphere or adsorbed on the surfaces of particles, has been appreciated. Although it has been known for many years that if certain glasses are allowed to cool in an atmosphere of burning sulphur, the surface properties are enhanced, it was not until 1940 that Hüttig¹ showed that sulphur trioxide could be adsorbed on the surface of glasses and so retard its reactivity and tendency to crystallise.

Hedvall² has shown that the reactions between the crystalline modifications of silica and lime are influenced by pretreatment with gases and he also proved that sulphur trioxide pronouncedly reduced the rate of reaction.

Small traces of adsorbed moisture or the presence of water vapour are known to catalyse certain reactions which would otherwise not take place. The role of water as a surface catalyst has been described in detail by Marshall, Enright and Weyl.³

Surface Phenomena. Within the last decade it has been established that the surface layers of a crystal are deformed and not to be compared in atomic arrangement with layers well within the crystal. Verwey, Stanski, Fajans, Weyl and others have recognised that many unusual properties exhibited by small-sized particles are due to the large surface area of distorted layers.

It is not within the scope of this book to detail the causes and implications of surface chemistry and how small crystals with large surface areas differ in reactivity from the classically represented structures. Briefly, it may be stated that the outermost ions or atoms of a crystal are not surrounded on all sides by 'screening' groups. The surface layers are, therefore, distorted and the electrical balance is not maintained. Hence, there is an increased possibility of reactivity or ease of combination with other chemical units in the immediate vicinity, and when reaction occurs it alleviates the insufficient surface 'screening'. (See p. 517.)

The *crystal growth* of many ceramic materials is attributed to the surface reactivity and so are many of the colloidal aspects of clay suspensions. The surface layers which behave as defective lattice structures often provide nuclei from which reactions can spread through the mass of a crystal.

The speed of reaction, is governed, in many cases, by the surface areas of reactants because it is only at the external, exposed faces that contact between reacting components can occur. Thus, a porous mass presents a much larger reacting

¹ Hüttig, G., *Z. anorg. Chem.*, 53, 35, 1940.

² Hedvall, J. A., *Trans. Brit. Ceram. Soc.*, 55, 1, 1956.

³ Marshall, P. A., Enright, D. P. and Weyl, W. A., *Proc. Int. Sym. on the Reactivity of Solids* (Gothenburg, 1952), Part 1, 273.

surface than the external faces of a solid body of similar dimensions and will usually be attacked more rapidly by liquid slags or corrosive gases.

Intimately linked with the surface layers of particles in a porous mass is the *angle of contact* or *surface tension* of fluids which may become associated with it. This, in turn, affects the chemical reactivity, for it governs the rate of penetration. If the corrosive liquid 'wets' the solid readily and penetrates the pores, the chemical attack will be much more rapid than if the fluid and solid were in less intimate contact.

Surface tension also has an important effect on physical changes in ceramic materials, particularly those relating to plasticity and slips (p. 474). Surface tension decreases with a rise in temperature but is increased by the addition of soluble salts. It is surface tension which causes water and other liquids to rise in capillary tubes and to penetrate ceramic and other materials, against the force of gravity. Water and mercury have a far larger surface tension than most liquids.

Crystallographic Structure and Properties. Reaction between solid materials is slow and proceeds by the diffusion of ions of one component through the other crystalline phases. The mechanism of diffusion is discussed in more detail later in this chapter, but it may be noted here that reactions of this type proceed more readily if the structure is open and contains a maximum of defects in the lattice.

Viscosity has an important effect on chemical action, because changes can only occur when the reacting substances are in intimate contact and a viscous material flows so slowly that it requires a long time to bring the reacting substances into contact. A mobile liquid will react much more vigorously than a viscous liquid with a solid (assuming other factors to be constant).

There are many reactions in ceramic processes which exemplify the effect of viscosity. Thus, slags at their fusing-point are often very viscous and exert little corrosive action upon the bricks with which they come in contact, but if the temperature is raised, many slags become quite mobile and then exert a powerful corrosive action as they flow more readily into the pores of the brick and so expose a greater surface to their action. Most alkaline silicates are very mobile when fused, and consequently, they readily combine with silica or fireclay. Magnesium and ferrous silicates are much more viscous, and as they flow more slowly and penetrate pores less readily, they are much less actively corrosive. Alumino-silicates are usually more viscous than simple silicates and are not generally so corrosive.

As vapours are still more mobile than liquids they may cause a serious amount of corrosion by penetrating into the smallest pores of bricks, etc., where liquids can reach only slowly.

The viscosity of slips and clay-pastes has a noteworthy effect on their behaviour.

The *solubility* of one of the reacting substances in the other or in a third substance usually increases the rate of reaction by bringing them into more intimate contact than would otherwise be the case. As most ceramic materials are insoluble in ordinary liquids, the chief case where solubility is concerned is that of the various substances in the fused material produced when the goods are in the kiln or are heated whilst in use. Such molten material—especially if rich in alkaline or calcareous silicates—has a powerful solvent action and will, in time, effect the destruction of almost all ceramic articles. It is to this action that the corrosion of

firebricks, crucibles, etc., by slags is due, and the same action is the cause of most of the distortion which occurs when ceramic materials are 'overheated'. As the fused material dissolves silica or other substances, it becomes increasingly viscous and eventually becomes saturated. After this has occurred, it loses its corrosive action so long as the temperature is not increased. Upon a rise of temperature, however, the equilibrium is destroyed and solution will continue until a new state of equilibrium corresponding to the higher temperature is established.

A very small solubility is sometimes sufficient to cause extensive chemical reactions, provided large masses or long periods of time are involved (see Law of Mass Action).

In certain solvents, of which water is a characteristic example, many substances dissociate into ions of unlike charge (see Chapter II). Chemical reactions which take place between solutions are generally regarded as proceeding through the interaction of ions, and in many cases the reaction cannot take place unless ions form. Thus, hydrogen chloride (HCl) dissolves in water to form hydrochloric acid which readily attacks limestone (CaCO_3); if, however, the gas is dissolved in dry benzene there is no interaction. The reaction is, therefore, said to proceed through the agency of hydrogen and chlorine ions into which hydrogen chloride dissociates when dissolved in water.

In the presence of water, many interesting reactions occur, particularly in connection with the flocculation of clays. Whilst these are mainly physical in nature, they also depend on the presence of soluble substances which are chemically active.

The solubility of the product of the reaction also affects the reaction (see Selective Action) as an insoluble product is largely removed out of the sphere of action and so prevents a reversal of reaction taking place.

Selective Action. Where two or more chemical reactions are possible, various conditions will determine which one will take place. If some of the substances present have different affinities for the remainder, the reaction will occur between those which have the greatest affinity for each other. If, by the interaction of two substances, present with several others, one possible product is volatile, that reaction which yields such a product will generally occur in preference to others which do not involve a change of state. Similarly, if one of the possible products is insoluble in the liquid under the prevailing conditions, the reaction which yields that product will usually take place in preference to any other reaction in which all the products are soluble. The presence of a catalyst (below) may also exercise a selective action.

In some cases, chemical action will not occur in the presence of weak acids or bases, but will do so when strong acids or bases are present. This action is termed *disposing affinity*. Thus, the oxides of such a substance may be difficult to form, and when formed may be readily decomposable, whilst the salts of strong acids or the salts produced by the action of strong bases may be quite stable. The precise cause of this mode of action is not known.

Selective action of components is important in determining the products formed on firing commercial magnesites or other basic materials, where the five common constituents are CaO , MgO , Al_2O_3 , Fe_2O_3 , SiO_2 . The preferential combination will be between the components exhibiting respectively the greatest alkalinity and the greatest acidity.

Catalytic Action. The presence of a small proportion of certain substances (catalysts) sometimes causes the interaction of two other materials, whereas without it no reaction would occur under the same conditions.

Indeed, many pure materials are known to be very inert although in the presence of a minute amount of impurity they react readily.

A *catalyst* or *catalyser* is (ideally) a substance which accelerates the rate of reaction but is unchanged itself, although in practice this rarely occurs. The most usual mechanism is for the catalytic agent to form an intermediate, transitional phase which then reacts to form the final product, thereby excluding the catalyst, which is restored to its initial state. The amount of catalyst which is required is often very small (a fraction of 1 per cent), so that it is difficult to investigate its precise action.

Water or water vapour is a frequent catalytic agent in many reactions. Thus, carbon monoxide and oxygen can be safely mixed without reaction taking place provided they are perfectly dry. The least amount of water, however, results in instantaneous and violent combination. 'Spots' of iron oxide catalyse the decomposition reaction of carbon monoxide into carbon and carbon dioxide. This reaction does not proceed to any great extent unless the iron oxide is maintained at about red heat as well as being in close contact with the gas. The reaction is then so active that if the iron spots are in a dense firebrick the carbon deposited may cause the brick to crack seriously.

Catalysts are also important in the conversion of quartz to other allotropic forms of silica. Oxides such as Fe_2O_3 , CaO , MgO , etc., greatly accelerate the transformation although, as will be described later in this chapter, the mechanism is such that it is doubtful whether the term 'catalyst' is strictly applicable.

Other catalytic reactions of importance in ceramics include the increase in the rate of crystallisation of periclase from raw magnesia in the presence of alumina or iron oxide.

Clays and diatomaceous earths are well-known catalysers of many reactions involving gaseous components. The large surface area provides nuclei at which reactions occur and when such 'spots' are exhausted, the catalytic activity is usually reduced and the surface is said to be 'poisoned'.

It should be clearly understood that a catalyst will not cause two substances to combine which could not otherwise do so; it merely facilitates the combination or the decomposition, as the case may be, by enabling it to take place under more convenient conditions than otherwise. So far as is known, all the reactions which are effected by the aid of a catalyst can take place without its aid, but only under conditions of temperature and pressure which are much more difficult to secure.

The *thermal conductivity* or ease with which a substance can transmit heat through its particles often determines the rate at which a chemical reaction or change in state can occur. Even an apparently small difference in thermal conductivity (such as that of fireclay bricks and silica bricks) makes a noteworthy difference in the retorts used for the decomposition of coal, zinc, blende, etc.

A low thermal conductivity may lead to undesirable results in a ceramic material containing a large proportion of an inverting material. This is particularly so where silica modifications of quartz, cristobalite and tridymite are present, for

these invert with large expansion effects. If the conductivity is low, parts of the material will undergo changes in length whilst others remain unchanged and disruption may result.

The *electrical conductivity* of the substances often affects the rate at which they react upon one another. If they are all non-conductors, any reaction which may occur will take place very slowly. In the presence of an electrolyte the rate of reaction will increase, and if all of the substances are electrolytes, the reaction will usually take place very rapidly. This is in conformity with the ionisation theory, which assumes that all substances are capable, under certain conditions, of splitting up into ions, each of which bears an electric charge (see p. 197).

Electrolytic changes include all changes in which an electric current is involved, including those in which an electric current is passed through a mass and those in which the particles are electrically charged even though no current has been applied.

The reactions in which an electric current is used are: (a) *electrolysis* or decomposition by current; (b) *kataphoresis*, or those due to the current separating one kind of particles from the others; and (c) those in which the electric current is merely a heating agent which eventually fuses a portion of the material and so enables reactions to occur which would not do so at a lower temperature; a typical example of this is the formation of carbides.

Changes in ceramic materials due to the passage of an electric current are of minor interest, as such materials are usually poor conductors of electricity.

The reactions which occur between electrically-charged particles in the absence of an obvious electric current are known as ionic reactions and they are very important in connection with the so-called colloidal properties as well as the acidic and basic properties of clays.

Light is a very important factor in many chemical reactions, such as those which take place in photography and in the oxidation processes occurring in plants and in other ways. The action of light on the chemical action of ceramic materials is not very marked, although sunlight is considered to facilitate the oxidation of impurities during the weathering of clays.

A change of state of one or more substances will often affect its power of reaction, especially if such change is accompanied by the formation of a liquid or gas. Many substances which do not react, or only slightly when in the solid state, will, if one or more is converted into a liquid (either by fusion or solution) or into a gas, react readily. Physico-chemical actions such as the production of solid solutions also occur more readily in the presence of a liquid.

Similarly, two relatively large pieces of material may remain in contact for some time without any appreciable reaction taking place, but if they are ground to a fine powder and then mixed, they may react readily. Thus, lumps of charcoal, sulphur, and nitre are fairly safe, but a powdered mixture of these materials in suitable proportions forms an explosive (gunpowder). The finer the particles of solid material the more readily will they react under favourable conditions. Conversely, if substances which are normally in the liquid or gaseous state are cooled, and so converted into a solid, their power of reaction is usually greatly diminished.

One of the chief reasons for heating solid substances which it is desired should react with one another is that the heating, if sufficiently intense, may cause a change

of state of one or more of the substances. Sometimes a small rise in temperature will greatly increase the intensity of chemical action.

The increase in chemical action which follows a change of state is almost wholly due to the greater ease with which the particles may come into contact with each other.

The *intimacy of association* or extent to which the particles are in actual contact with each other is a highly important factor. It is generally agreed that unless the atoms (or ions) of reacting substances come within a very minute distance of each other, so as practically to be in contact, no reaction can occur. In most cases, actual contact appears to be essential, and the greater the area of the surfaces of the materials in contact the greater will be the speed of the reaction. Consequently, the intimacy of association is dependent upon (a) the shape of the particles, (b) the size of the particles, (c) the homogeneity or heterogeneity of the mixture, i.e. the extent to which they are mixed together, (d) the porosity in the case of massive materials, and (e) the area of surface in actual contact.

If the particles are small and are in the form of thin flat plates, needle-shaped crystals or other shapes with a large surface area and a very small cross-sectional area, reactions will take place more rapidly than with more compact pieces such as spheres, as the former present a greater surface for the same mass of substance and, consequently, they can enter into more intimate contact. For this reason, thin flakes of mica are more harmful as an impurity in clays than the more compact grains of felspar.

If the area of contact between two materials is increased by compressing them (see Pressure, p. 527), the possibilities of chemical reaction will be correspondingly increased.

The *relative quantities of the reacting substances* exert an important influence on the extent to which a chemical reaction can take place, and if large quantities are involved, the result may be quite different from that obtained with small quantities. This difference is due to a variety of causes, such as the much greater heat required to permeate the centre of a large mass of low conductivity and the consequent slower rate of reaction of large masses.

If a material is in large compact pieces of approximately cubic or spherical shape, the rate at which they can react and the extent to which the reaction can proceed must be very small, unless the conditions are such that the products of the reaction are removed as soon as they are formed. Thus, iron filings can be completely oxidised by steam only when a very large surface of iron is exposed, and conversely, iron oxide can be reduced completely to metallic iron only when a very large volume of hydrogen—much in excess of that actually needed to combine with the oxygen—is present. The mass of the available materials appears to affect the reaction quite apart from the penetrability of the solid material concerned. Thus, a typical example of mass action is shown by the fact that, whilst many silicates are unaffected by powerful acids in the laboratory, they are readily decomposed by feeble acids (such as a solution of carbon dioxide in water) when exposed in large quantities, as in the 'weathering' of natural rocks.

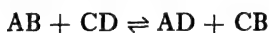
What is sometimes termed the *law of mass action* states that broadly a reaction will proceed further or more easily if the mass of one of the reacting substances is in

excess, but the results in any given case are subject to various other factors, such as those mentioned in the preceding pages. Not only the total mass, but the relative proportion of the product exerts an important influence on the progress of the reaction.

STATES OF EQUILIBRIUM AND THEIR DISTURBANCES

WHEN a material is 'at rest' both chemically and physically it is said to be in a state of equilibrium. This state can be destroyed by various means of which heating is one. When such a disturbance occurs, there is always a tendency for a fresh equilibrium to be established. This is particularly the case when the disturbance starts a chemical reaction between two or more substances or on the withdrawal of one or more of the interacting substances which maintain the equilibrium.

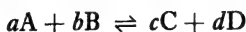
The Law of Mass Action. Berthollet (1799) pointed out that a chemical reaction does not only proceed in one direction ('to the right') but may do so in the opposite direction ('to the left'). Thus the equation: $A + BC = AB + C$ may proceed only to a certain extent because the opposed reaction $AB + C = A + BC$ can occur under the same conditions and at the same time. A state of equilibrium is then reached in which the opposing reactions balance each other and proceed at equal speeds. Thus reversibility is denoted by substituting the sign \rightleftharpoons for the customary sign of equality ($=$) as in



Berthollet also showed that the extent to which a reaction proceeds depends on the concentration of each of the reactants present in a given volume and, that if an excess of one reactant is added to a mixture which is in equilibrium, the concentration of that reactant will be reduced.

The Law of Mass Reaction (Guldberg and Waage (1864-7)) states that the extent to which a substance reacts is proportional to its concentration and therefore to the products of the concentrations of each of the reactants.

When representing this mathematically, it is customary to use the chemical symbol for each reactant, enclosed in square brackets, to represent one gram molecule (mole) so that $[A]$ represents one mole of A whilst the symbols $a, b, c, d \dots$ represent the number of moles in the reaction. The state of equilibrium is then represented by



and the extent to which a reaction can proceed is proportional to the products of the reactants, i.e.

$$\frac{[A]^a}{[B]^b} = \frac{k[C]^c}{[D]^d}$$

where k is always constant for a particular reaction.

If only one gram molecule of each reactant is involved, $a = b = c = d = 1$ and the ratio of the concentrations of the reactants to that of the products is always constant.

The velocity of the reaction towards the right represented by V_1 is related to the partial concentrations of the reactants by the relationship:

$$V_1 = k_1[A]^a[B]^b$$

Similarly if the reaction is reversible there will be a positive velocity V_2 to the left, viz.:

$$V_2 = k_2[C]^c[D]^d$$

At equilibrium

$$V_1 = V_2$$

hence

$$k_1[A]^a[B]^b = k_2[C]^c[D]^d$$

or

$$\frac{k_1}{k_2} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

As k_1 and k_2 are both constant terms the Law of Mass Action can be stated in general terms as¹

$$\frac{[A]^a[B]^b}{[C]^c[D]^d} = K$$

The law of mass action may be used to control the results of chemical reactions. If, for example, it is desired to increase the amount of C at equilibrium it can be done in three ways: (i) by increasing the amount of A; (ii) by increasing the amount of B; and (iii) by decreasing the amount of D.

The law of mass action applies to all chemical reactions, but it is sometimes difficult to use because the 'active mass' of one or more of the reacting substances cannot be determined with sufficient accuracy.

Although the implications of the Law of Mass Action are quite general they apply more particularly to reactions which take place in solution. When gas is formed from a solid phase a different condition arises. Thus in the system



if the vapour pressures of the components are a , b and c respectively, then, since the concentrations are proportional to the pressure,

$$K = \frac{bc}{a}$$

but a and b are constant because they relate to solid CaCO_3 and CaO , hence the equation becomes

$$K = c$$

Hence the pressure of CO_2 has a fixed value at every temperature. This is known as the dissociation value of CaCO_3 .

According to Guldberg and Waage, 'in a system of reacting bodies, the effect of each substance is proportional to its concentration, and the velocity of the reaction is proportional to the product of the molecular concentration of the reacting substances'.

$$\text{i.e. } V = k[A]^a[B]^b$$

¹ The constants k_1 and k_2 are termed *velocity constants* and K is the *equilibrium constant*.

where V = velocity of reaction, A and B are the molecular weights of the reactants (in gm.) a and b are the amounts of the products of the reaction and k is a constant.

Mass action plays a very important part in some processes connected with the ceramic industries; in the formation of some of the raw materials, it enables weak acids to do what cannot, on a small scale, be accomplished by much stronger acids (see p. 534). It largely determines the progress of reactions involving the decomposition of rock masses by water, such hydrolysis occurring in accordance with the law of mass action and its extent depending on the equilibrium expression and the concentration of the ions of the reacting substances.

In the case of the substances produced by methods of manufacture or during the use of ceramic materials, the final products are largely dependent on the effect of mass action, as the temperatures to which ceramic materials are heated are seldom sufficient to produce complete fusion, in which state the reactions between the various substances take place with the greatest rapidity. Consequently, the reactions are seldom complete and their progress depends upon the temperature and duration of the heating, as well as on the quantities of the various materials employed. In a thin tile or vase exposed on all sides to the heat of the kiln, the amount of fused material and of the various reaction products will be much greater in proportion to the size of the article than they would be in a solid cubic mass of the same material having the same total volume, because the heat will penetrate the former article much more readily than the latter. In this case a change in the shape of the mass has the effect of delaying the progress of the reaction.

In solid systems, the law of mass action still applies although it is usually not possible to apply it in the strictest sense. The overall concentration of one component in the mass may be very small but if it is present in discrete particles, the localised concentration over a small area may be very great. Hence the products in such regions may be totally unpredicted yet they may play a large part in determining the properties of the mass.

REVERSIBLE AND IRREVERSIBLE REACTIONS

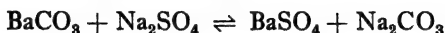
THE terms reversible and irreversible reactions are used to denote chemical reactions which will or will not proceed in opposite directions when the relative masses of the reacting constituents are changed. In an *irreversible* reaction, the products cannot by any simple change in conditions, such as by varying the temperature or adding an excess of one of the products, be reconverted into the original materials which existed prior to the reaction taking place. Thus, oxidation reactions involving complete destruction of the original substance, as with sugars and other organic materials, may be termed irreversible.

Many reactions which were formerly thought to be irreversible are now known to be otherwise, e.g. the decomposition of kaolinite at moderately high temperatures.



which is strictly reversible, for kaolinite can be reformed provided that the pressure of water vapour is sufficiently high. Under normal conditions, however, the reaction may be regarded as irreversible.

In a *reversible* reaction, on the contrary, the original substances may be reformed by a simple change in the conditions or in the proportions of the products. Thus, when a chemical action occurs and the products of the reaction are not removed, a certain point of equilibrium may be reached at which the action may proceed indifferently in either direction, though no equilibrium-point may be apparent at ordinary temperatures. For instance, at 100° C., the reaction between barium carbonate and sodium sulphate is reversible:



The system is in equilibrium when there are five parts of sodium carbonate to one part of barium sulphate. With greater concentrations of barium sulphate the latter is decomposed, and with smaller concentrations barium carbonate is decomposed. Thus, in a solution of these salts, either heavy spar or witherite may be deposited, according to the relative proportions of each and the temperature of the solution.

The action of heat upon calcium carbonate also involves a reversible reaction:



The dissociation of the calcium carbonate occurs only when its dissociation tension exceeds the vapour pressure of the carbon dioxide present in the system. As soon as the latter becomes greater than the former, lime and carbon dioxide recombine to form calcium carbonate.

Numerous reversible reactions occur in Nature, many of which are of special interest in connection with ceramic materials. The well-known silica inversions and conversions are typical examples.

The Le Chatelier-Braun Principle. The maintenance of a state of equilibrium does not depend only upon the law of mass action. As stated in the Le Chatelier-Braun principle (1884) if *any* factor in a reaction is changed, the whole system will tend to form a fresh state of equilibrium and so annuls the disturbing effect, either partially or completely. In other words the state of equilibrium in a system of reactants and products depends on the relative concentrations, on the temperature, pressure and possibly other variable conditions.

Whenever a reversible reaction can occur and the products of the reaction cannot escape, the condition of equilibrium persists and such a reaction may, therefore, be termed a *balanced reaction*.

The distribution of the reacting masses, when in equilibrium, is determined by the relative concentration of the changing substances, as previously explained.

Until comparatively recent times the existence of equilibrium reactions was unknown; at present the tendency is to regard all reactions as equilibrium reactions, and that even where they appear to be complete, to consider them as only in apparent completion, i.e. in reality, the equilibrium merely lies so far to one side as not easily to be disturbed. If this view is adopted, it will be seen that balanced or equilibrium reactions are especially common in the case of ceramic and other materials which may exist in two or more allotropic forms such as silica, magnesia, etc., the particular form present being then largely dependent on the temperature and pressure. Balanced reactions are equally important in the case of many ceramic products.

especially those in which a considerable amount of vitrification has occurred, as in porcelain, stoneware, etc., and in glazes, because the composition of such material depends very largely on the nature of the mixture and its state of equilibrium. This subject is of the greatest importance and is known as *Phase Equilibria*.

PHASE EQUILIBRIA

WHEN two or more substances are brought into contact, reactions may occur which result in the formation of entirely different chemical entities. The final products will depend on many factors such as the concentration and intimacy of mix of the reactants and the temperature at which the reaction proceeds.

Many physical and chemical changes progress at a finite rate and eventually reach a state of *equilibrium*. A *phase equilibrium* is the final steady state of reacting materials under specific external conditions.

In order to describe a set of reactants and products, the following terminology is usually accepted:

A **System** is the whole of the chemical field under investigation and comprises all the reactants and products under given equilibrium conditions.

A **Phase** is defined as any portion of a system which is physically homogeneous within itself and is bounded by a surface so that it is clearly separated from other parts. Thus, matter which is known to exist in three forms, solid, liquid and gaseous can, under certain conditions, exist in all these three phases. The compound, expressed simply as H_2O , can be solid (ice), liquid (water) or gaseous (steam, water vapour) depending on the conditions under which it is examined. A mixture of substances may form a single phase; sodium chloride dissolves in water, for example, to form a homogeneous, single phase solution. Many liquids are mutually soluble to give a single phase system; alcohol and water mix readily, whilst oil and water is an example of two liquids which do not mix and hence form two phases.

Components are the smallest number of independent variables by which the composition of a mixture may be conveniently expressed. These may be elements, oxides or more complex compounds depending upon the simplicity or otherwise of the system. In ceramic studies, the individual units are usually oxides. The reason for this is more obvious if a system containing calcium, silicon and oxygen is considered. If elements were to be regarded as the basic components, then three composition variables are permissible, viz. calcium, silicon and oxygen. As it is known that the oxygen content under normal conditions is always governed entirely by the relative amounts of calcium and silicon (the total amount being expressed as $CaO + SiO_2$), the oxides are more conveniently regarded as the basic components and thus only two composition variables (lime and silica) are involved. Where an element of variable valency is present, such as Fe, it may be of advantage to consider oxygen as a separate component.

The degrees of freedom or variance in a system are the number of independent variables which must be fixed before the system can be clearly defined. In general, only three factors are involved and these are temperature, pressure and concentration. **Equilibrium** exists when the phases do not undergo any further change either in type or amount, under the fixed conditions.

The conditions at equilibrium in any system of components may be accurately forecast by the Phase Rule—deduced by Willard Gibbs—in accordance with which the number of phases that can exist in any system is limited and given by the equation:

$$P + F = C + 2$$

where P is the number of phases, F is the number of degrees of freedom, and C is the number of components.

As a simple illustration, the *single component system* H_2O contains only one component and the equation may be reduced to:

$$P + F = 1 + 2 = 3$$

If one phase is present, the number of degrees of freedom is 2: i.e. the system is bivariant. In other words the temperature and pressure are completely independent variables.

Now if two phases are present then $F = 1$ and the system is univariant. If the phases present are to be kept the same, the alteration of one variable must be accompanied by an equivalent alteration in each other variable. This would be the condition where liquid water is in equilibrium with vapour, as it is over the range $0-100^\circ\text{C}$.

If three phases, solid, liquid and vapour are all present then $F = 0$; i.e. no degrees of freedom are permissible. The system is *invariant* at such a *triple point*. Should the slightest change occur in the conditions of the system, i.e. in the temperature or pressure, one of the phases must disappear.

In the ice-water-steam system there is only one component, but Gibbs' rule is equally applicable where there are several components. Thus, the conditions of equilibrium of calcium carbonate involve three phases, namely, solid (calcium carbonate), solid (lime), and gaseous (carbon dioxide), so that calcium carbonate forms a three-phase system. Calcium carbonate may be resolved into two components—calcium oxide and carbon dioxide—so that $C = 2$, and on substituting this in Gibbs' rule, the equation becomes

$$P + F = 2 + 2$$

i.e.

$$P + F = 4$$

If only one condition is fixed, i.e. $F = 1$, then $P = 3$, and the three phases can exist only at one definite temperature or pressure. For example, at 600°C . and at all pressures, all three phases can exist simultaneously; but if both the temperature and the pressure are fixed, $F = 2$ and $P = 2$, only two phases could exist under those conditions.

Granite, composed of quartz, felspar, and mica, has three components (alumina, silica, potash) and three solid phases (mica, quartz and felspar). It is, therefore, univariant. It is also in equilibrium because, not being at a transition-point, it can survive small variations in temperature without changing the state of the system.

The phase rule is very valuable because:

1. It permits the classification of systems of similar behaviour.
2. It shows whether the phases of a heterogeneous system are those necessary for equilibrium.

3. It assists in identifying chemical individuals among a series of basic salts or solid solutions.

Gibbs' rule is capable of very wide application and is not limited by the complexity of the factors represented by the symbols P, C, and F. It is, however, qualitative rather than quantitative in its nature, because it does not show which phases will occur, where only a limited number are possible, and it only states the maximum number of phases which could possibly occur. Its value is, therefore, limited to showing the maximum value for each of the symbols P, C and F in any system. When the particular nature of the factors represented by the symbols is required to be known, another method must be adopted, namely, an equilibrium diagram or phase diagram.

The chief value of the phase rule consists in its power of indicating the maximum value of one or more of the symbols in a given system. In some cases, where this value is unity, no further investigation is necessary, but if, for instance, the rule is employed to determine how many phases can occur in a given system and that number is greater than unity, the use of a phase diagram may be essential if it is desired to ascertain the nature of the possible phases.

The chief difficulty experienced in using the phase rule lies in ascertaining what are the precise components, as, in complex cases, their nature is very difficult to determine.

EQUILIBRIUM OR PHASE DIAGRAMS

AN equilibrium or phase diagram is one which shows what phases can exist under given conditions. In any one given system, all equilibrium conditions can be referred to three possible variables, namely temperature, pressure and composition. In simple cases, e.g. a single component system, two variables only need be considered, hence a plane diagram with pressure and temperature as the two axes will completely describe the system. These can conveniently be regarded respectively as the *ordinate* (vertical axis) and *abscissa* (horizontal axis) of a plane diagram.

ONE-COMPONENT SYSTEMS

A GENERAL form of the diagram is shown in Fig. X.1, where the solid form of the component can exist in two modifications A and B. Solid modification A can exist in equilibrium with vapour along the line WX, which is called a *phase boundary line*. At any point along its length two phases can be present, hence by reference to the phase rule F must equal 1, i.e. the system is univariant.

This is also the condition along the other phase boundary lines shown in the diagram. There are also two *triple points* at W and Z. At such positions three phases can exist simultaneously, hence the number of degrees of freedom if the phase rule is to be obeyed must equal 0. The points W and Z are known as *invariant points* because neither the temperature nor pressure can be altered without causing one phase to disappear.

One component systems are not of great importance in ceramic studies, although a notable example is that of *silica*, SiO_2 , the phase diagram of which is shown in

Fig. X.2. Both the inversions and conversions are shown and the dotted portions represent the unstable phases under equilibrium conditions.

In systems where there is more than one component, the construction of phase equilibrium diagrams becomes more complex. A two-component mixture requires an additional axis before it can be described completely, and as the number of components increases, so does the difficulty of representation.

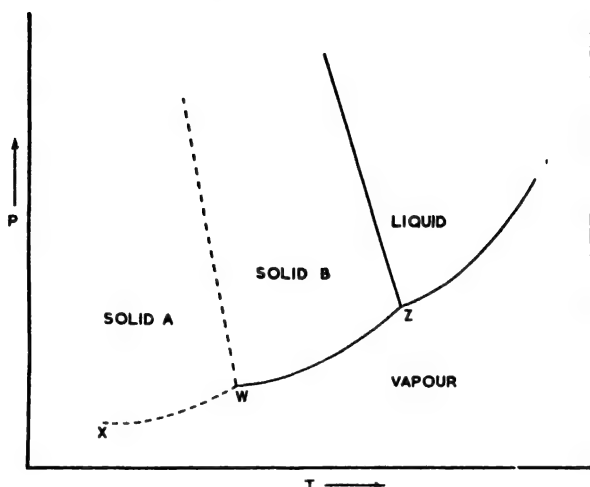


FIG. X.1. PHASE DIAGRAM OF A ONE-COMPONENT SYSTEM SHOWING TWO SOLID MODIFICATIONS, A LIQUID AND A GASEOUS PHASE

Reactions between ceramic materials, however, usually involve only solid and liquid phases. The gaseous state is of little consequence and for most purposes can conveniently be disregarded. Such 'condensed' systems no longer have vapour pressure as a variable or degree of freedom hence a modified form of the Phase Rule can be applied to predict the possible phases. This is written:

$$P + F = C + 1$$

where once again, P is the number of phases possible, C is the number of components, and F is the number of variables or degrees of freedom.

TWO-COMPONENT OR BINARY SYSTEMS

IN mixtures of two components ($C = 2$) the degrees of freedom compatible with the number of phases present may be predicted from the condensed phase equation thus:

when	$P = 1$	$F = 2$
when	$P = 2$	$F = 1$
when	$P = 3$	$F = 0$

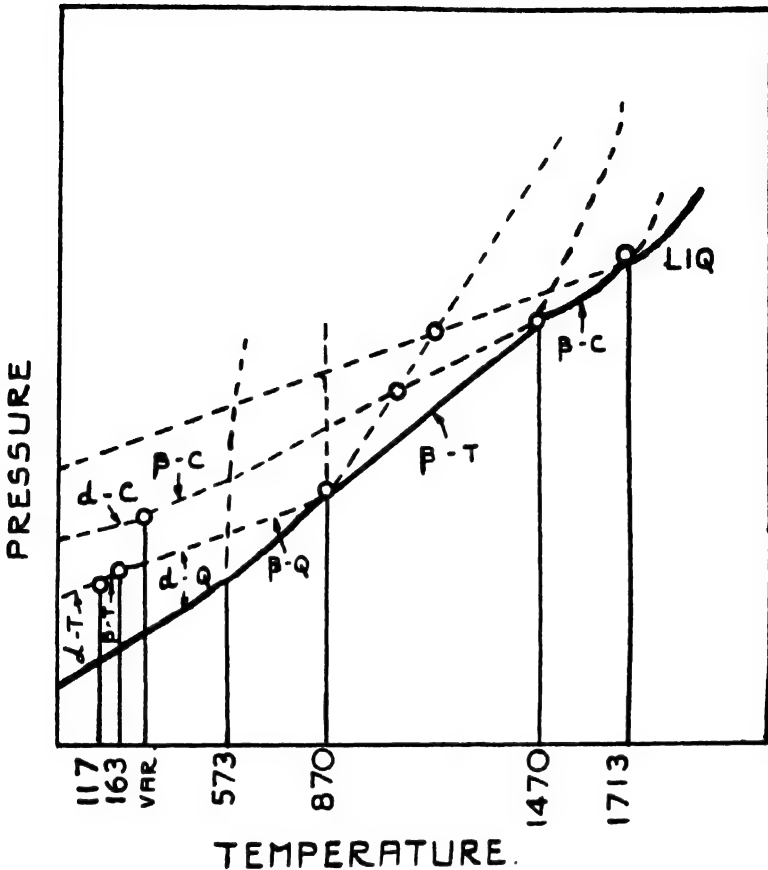


FIG. X.2. THE PHASE RELATIONSHIPS OF SILICA

There are only two variables to consider namely temperature and composition and as the latter can be represented by one axis, a simple plane diagram can be constructed with temperature as the ordinate and composition as the abscissa. Any mixture of two components can be represented by a point along the horizontal axis.

Interaction between two components may be of more than one type and consequently several equilibrium diagrams are obtained which may be divided into four general classes as follows:

1. Where the two components do not mix (immiscible) in either the solid or liquid states.
2. Where the components are completely miscible in the liquid region, but are immiscible in the solid phase.
3. Where compound or complex formation between the two components takes place.

The depression of the freezing point is thus independent of the nature of added substance and is a solvent characteristic, provided that the solvent does not form crystalline or solid solutions with the added phase, but separates in a pure form.

As increasing amounts of A are added to B the temperature at which initial crystallisation begins falls progressively along the line T_1E (see Fig. X.4). Similarly, additions of component B to A, cause a lowering of the melting point of A along the line T_2E .

At all points on the line T_1E solid component B is the only phase to crystallise. Along T_2E , only solid A can be formed. At the point E, however, which is the lowest temperature at which liquid can be present, both solid A and B crystallise together. Three phases can now be theoretically present, liquid, solid A and solid B. Hence, this must be an invariant point because, as predicted by the phase equation, the number of degrees of freedom is zero, and, before the temperature can be altered, one phase must disappear. The point E is termed the *eutectic point* of the system.

The system is more clearly appreciated by considering the changes which occur on cooling a specific mixture, such as M, which is a mixture rich in component A. Above the liquidus line, only one phase is present but on cooling to the temperature (T_3) the composition line of the mixture meets the phase boundary line T_2E . Solid component A begins to crystallise. At this point (C), two phases are present, hence the degree of freedom predicted by the 'condensed' phase equation can only be 1, i.e. the system is univariant.

As crystalline A separates, the liquid phase remaining becomes richer in component B and its composition follows the line T_2E .

This progressive crystallisation of solid A and the alteration of the composition of the liquid phase continues until the temperature T_5 is reached, at which point the liquid remaining has a composition corresponding to E. Solid B must also separate at this temperature and the temperature must remain constant until all the liquid phase vanishes. The system then contains only two solid phases which do not undergo further alteration on cooling.

At any temperature above the eutectic point the relative amounts of liquid and solid phase may be assessed by applying the 'lever' rule. At a temperature T_4 , for example, which is between the temperature of initial (T_3) and final (T_5) crystallisation, a certain amount of solid A will have crystallised and the liquid remaining will have the composition indicated by the point D. If a horizontal line is drawn across the diagram at the temperature T_4 cutting the mixture composition vertical at N, then the ratio of solid to liquid is given by the relative lengths of ND and T_4N . That is

$$\frac{\text{amount of solid A}}{\text{amount of liquid (composition D)}} = \frac{\text{length of ND}}{\text{length of } T_4N}$$

The cooling of a liquid of composition M results in progressive crystallisation. Conversely if a solid mixture of the composition M were heated some liquid would be formed at the eutectic temperature T_5 . The amount would be predicted by the lever principle as

$$\frac{\text{amount of solid A}}{\text{amount of liquid (composition E)}} = \frac{\text{length OE}}{\text{length of } T_5O}$$

Similar conditions of solidification would be observed in a liquid mixture rich in component B. The phase to crystallise would, in this case, be solid B, and the liquid phase would become progressively enriched with A. No solid A could separate until the eutectic temperature (T_E) was reached, when instantaneous solidification of all remaining liquid would take place.

In the interesting case of a mixture with a composition corresponding to that of the eutectic E, the single liquid phase would persist at all temperatures above T_E . At this temperature, however, three phases can co-exist and the system is invariant, requiring that the temperature must remain constant until one phase vanishes. Hence, complete crystallisation can take place at one temperature or, on the reverse cycle, a definite melting point would be observed. This is one of the few cases known in ceramic materials where a mixture may be said to have an established, single melting point.

3. **Compound or complex formation** of three types is known, each of which has a distinct phase equilibria diagram.

A. When a compound is formed which decomposes below the eutectic temperature of the two components, the equilibrium diagram is as shown in Fig. X.5.

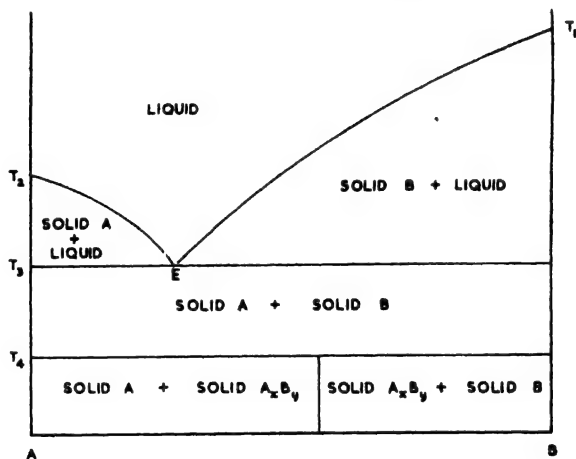


FIG. X.5. A BINARY MIXTURE WHERE A COMPOUND FORMS WHICH IS DECOMPOSED BELOW THE EUTECTIC TEMPERATURE

The changes between compound A_xB_y and the components A and B all occur in the solid state and as the temperature is raised above T_4 , the complex decomposes into its equivalent amounts of A and B.

B. A compound may be formed which decomposes before melting, but at a temperature above the eutectic point. This is known as incongruent melting and a peritectic point (P) is produced as in Fig. X.6.

In the two-component system of A + B, the compound A_xB_y is stable in all solid mixtures. On heating to T_p , however, the compound dissociates into a liquid phase (P) and crystals of component B.

The cooling phenomena of three mixtures more clearly illustrate the salient features of the diagram. These are mixture L (richer in B than the compound A_xB_y), mixture M (of the composition A_xB_y) and mixture N (with an excess of A over A_xB_y). All are liquid at points above the phase boundary line T_1P but begin to crystallise at the temperature where the composition line intersects the liquidus line.

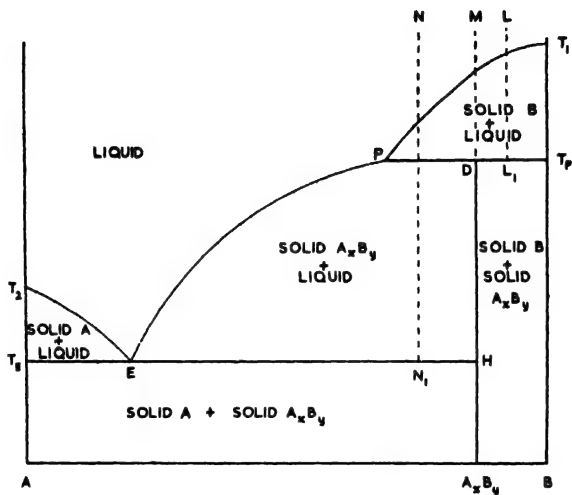


FIG. X.6. A BINARY MIXTURE CONTAINING A COMPOUND WHICH DISSOCIATES BEFORE MELTING, BUT ABOVE THE EUTECTIC TEMPERATURE

Solid B is first formed in all cases and continues to crystallise whilst the liquid composition follows the path of the phase boundary line T_1P . As the temperature reaches T_P , the solid component B which has already formed, begins to redissolve in the liquid of composition P and at the same time the compound A_xB_y is crystallised. The point P is thus invariant and the temperature must remain constant until one phase disappears.

In mixture L, solid B is not completely redissolved before all component A in the liquid phase combines to form the compound A_xB_y ; so the liquid phase vanishes and the solid system contains crystals of A_xB_y and also B. The relative proportions of the two solid phases are given by applying the lever principle around L_1 with the composition line A_xB_y as one extreme and the B ordinate as the other, i.e.

$$\frac{\text{amount of solid } A_xB_y}{\text{amount of solid B}} = \frac{L_1T_P}{DL_1}$$

In mixture M there is just sufficient liquid phase, containing component A, to redissolve the solid B and precipitate a new solid phase consisting entirely of the compound A_xB_y .

Mixture N is richer in A and therefore after all the originally-crystallised B has been redissolved with formation of solid compound A_xB_y there is still some liquid

phase remaining. The temperature can be further reduced with more solid A_xB_y crystallising whilst the liquid composition follows the phase boundary line PE. Some liquid remains until the eutectic temperature T_e is reached, when simultaneous precipitation of compound A_xB_y and solid A takes place. The relative amounts of the two solid phases below the eutectic temperature may again be calculated by applying the lever principle around the composition line N.

$$\frac{\text{amount of compound } A_xB_y}{\text{amount of solid A}} = \frac{T_e N_1}{N_1 H}$$

If a mixture with a composition between E and P were cooled from the liquid state, the first crystallisation product would be compound A_xB_y , and this would be the only solid phase until the eutectic temperature, when solid A would also form.

Mixtures between pure A and the eutectic composition E crystallise solid A initially and then simultaneously solid A and compound A_xB_y at the eutectic temperature.

The formation of a compound with an incongruent melting point is a feature of the alumina/silica diagram (see Fig. X.17, p. 562), where mullite $3Al_2O_3 \cdot 2SiO_2$ dissociates at 1810°C. into corundum ($\alpha - Al_2O_3$) and a liquid phase.

C. When the compound is stable at all temperatures and melts congruently the phase diagram has the form shown in Fig. X.7.

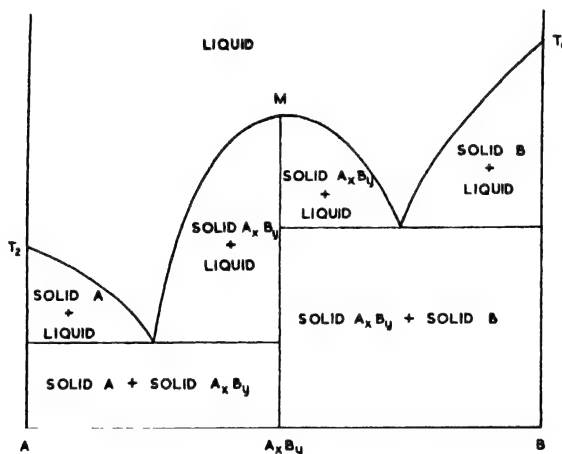


FIG. X.7. THE PHASE DIAGRAM OF A BINARY MIXTURE WHICH FORMS A CONGRUENT COMPOUND

The diagram is characterised by a maximum in the phase boundary curve corresponding to the composition of the compound A_xB_y . For most purposes, such diagrams may conveniently be separated into two parts divided by the composition line A_xB_y . It will be seen that the parts have each the form of a simple binary mixture with a eutectic point; the components of the systems are A and compound

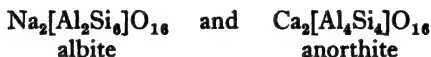
A_xB_y and B and compound A_xB_y respectively. All the laws of crystallisation and melting which apply in the binary system where the two components are immiscible in the solid state, are also operative in this case.

If the pure compound A_xB_y is heated it will melt at M, which is an invariant point, because the system contains only one component (the compound itself) and hence two phases give rise to no degrees of freedom, as predicted by the condensed Phase Rule.

4. Two components miscible in both liquid and solid states. In such systems both the solid and liquid phases are homogeneous and the two components form solid or crystalline solutions.

A solid solution is where two crystalline substances merge their chemical entities. Three examples are known:

(a) Where two crystalline materials of similar habit and lattice dimensions form a single crystal. Such an example is the mineral dolomite which is a double carbonate of calcium and magnesium. The crystal habit and lattice of dolomite are not unlike those of the single carbonates, the only difference being that calcium and magnesium cations are both present in the lattice at the same time and are mutually interchangeable. The compound must not be confused with a mixture of the two components. Each part of the crystal is identical with all other parts. The formula of dolomite should be written $(Ca.Mg)CO_3$ and not expressed as a mixed carbonate. Solid solution of this kind is very common in ceramic minerals; the spinels, olivine and many common slag minerals are typical examples and even substitution in montmorillonite and micaceous minerals may be so regarded. Ideally, this type of crystalline solution will most readily occur when the interchangeable components or ions are almost identical in size and charge. This is usually the case, but there are many anomalies; for example, one of the best known naturally-occurring solid solutions is the plagioclase feldspars, where the interchange is $(Na^+ + Si^{4+})$ for $(Ca^{2+} + Al^{3+})$. A whole series of minerals is known between the two extremes:



(b) Where foreign ions are contained in holes or defects within the crystal lattice of a mineral. Occasionally, two entirely different crystalline components form solid solutions, but usually in only a limited range of composition. Ionic substitution or replacement is impossible yet the foreign ion is held firmly within the lattice.

Little is known of this kind of solid solution, but its formation has been established with certainty. The formation of such complexes is most common when the crystalline structure is open. This is the case in silicates which are based on the framework structure (see Chapter III) and it is here that solid solutions of this type are most common.

(c) Diffusion-type complexes. Many solid substances, when placed in contact with others, will slowly diffuse into the crystal lattice of the other component. This process is usually greatly accelerated at high temperatures and the extent of penetration may, in some cases, cause a breakdown in the crystal lattice. The complex formed may be random in structure with dissimilar ions occupying equivalent

positions in the same lattice. Eventually, such diffusion-type complexes may lead to compound formation, but, in the initial stages, they have all the characteristics of true solid solutions.

Although they may be extremely variable in composition, solid solutions are not to be confused with glass. Unlike the latter, they have all the properties of true crystalline solids. On the other hand the term solid solution does not imply compound formation where the combination of components is in a fixed invariable stoichiometric ratio. The term infers that one solid phase is incorporated into another in such a way that a continuum or single phase is formed in which the properties of the parent substances are modified, but not completely changed. The main distinction between a solid solution and a compound is that the melting point in the former extends over a range of temperature whilst in the latter it is usually sharp. There are, however, exceptions to this rule, for some well-defined compounds are known which decompose in the solid state and so have an extended melting range.

The simplest equilibrium diagram for components with a complete range of solid and liquid solution is illustrated in Fig. X.8. There are two phase boundary lines; the upper of which is known as the liquidus and represents the maximum temperature at which solid phase can exist at all compositions; the lower curve or solidus indicates the minimum temperature at which liquid can form in any particular mixture.

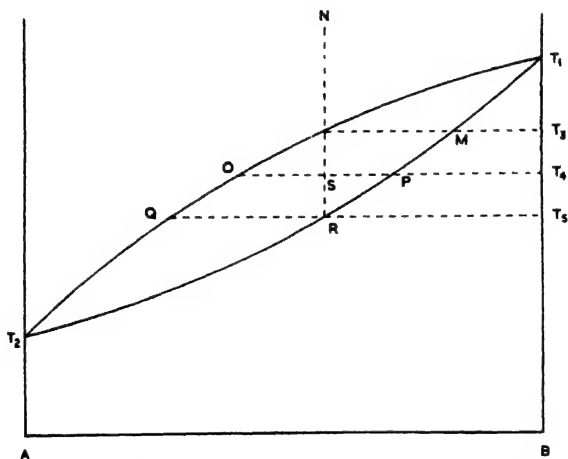


FIG. X.8. THE PHASE DIAGRAM OF A BINARY MIXTURE WHERE THE COMPONENTS ARE COMPLETELY MISCIBLE IN BOTH THE LIQUID AND SOLID FORM

The addition of component A (of lower melting point) to component B depresses its melting point, although amounts of B increase the melting temperature of A.

The region between the two phase boundary lines is known as the field of heterogeneous melting where liquid and solid phase can exist together. The extreme

ends of the horizontal lines, known as *tie lines* (e.g. OP and QR), drawn across this region represent the composition of the liquid and solid phases which exist in equilibrium with each other at particular temperatures.

The phases which form on cooling are clearly indicated by a mixture of composition N which, when cooled from a temperature above the liquidus line, has a single uniform phase until the temperature T_3 is reached. Crystallisation commences, but the solid phase first formed has a composition represented by the point M, i.e. richer in the component of higher melting point than is the initial mixture. At this point only two phases are present hence the system is univariant and the temperature can be progressively lowered.

As the cooling continues, the composition of the liquid phase changes (due to crystallisation of an excess of component B), and follows the path of the liquidus curve. At temperature T_4 for example the liquid has the composition of the point O. The solid which is in equilibrium with this liquid has the composition given by the point P, the point of intersection of a horizontal line through O and the solidus phase boundary curve. Hence, not only does the liquid phase change in composition as the temperature is lowered, but so does the solid being crystallised. Ideally, if the rate of cooling were sufficiently slow, the solid phase formed would constantly be re-dissolved and recrystallised with an ever-changing composition. This cooling process would continue with more solid being formed of a progressively increasing concentration of component A until the temperature T_5 was reached. Here liquid of composition Q is in equilibrium with solid R and as R is along the *isopleth* (line of constant composition) of N, all liquid must disappear and only a solid solution of uniform composition will be present.

The relative amounts of liquid and solid phase at any stage of the crystallisation are given by applying the 'lever principle' about the point of initial composition. At T_4 for example, liquid O is in equilibrium with solid P, and the relative amounts of each are expressed as

$$\frac{\text{amount of liquid O}}{\text{amount of solid P}} = \frac{PS}{SO}$$

Thus at the temperature T_5 the amount of liquid of composition Q will be infinitesimal.

Systems of two completely miscible components in both the liquid and solid states are common in both rock-forming minerals and in slag compositions. In general, such mixtures do not cool sufficiently slowly to allow equilibrium to be attained at all temperatures. In some igneous rocks there is evidence that, although cooling may have extended over a geological age, there has been insufficient time for the resolution and solid diffusion reactions to proceed to completion and form homogeneous crystals. Many minerals which occur in eruptive rocks exhibit characteristic *zoning* or *fractional crystallisation* and this phenomenon is even more common in the typical silicate minerals found in slags.

The formation of zoned structures is clearly demonstrated by considering the cooling of a mixture of composition N (Fig. X.8), but under more rapid non-equilibrium conditions. Once again crystallisation begins at a temperature T_3 and the composition of the first solid phase to appear is represented by the point M. The

liquid phase becomes deficient in component B and its composition follows the path of the liquidus curve. If conditions were ideally those of equilibrium cooling, the solid phase would be constantly changing in composition due to resolution and recrystallisation or to solid diffusion, but, under practical conditions, these processes do not proceed rapidly enough and crystallisation of material of ever-changing composition continues with the original deposits acting as seeds for later crystallisation. This process continues until all the liquid disappears with the result that the final solid consists of zones of material, the centre core of which is comparatively rich in component B but with the composition changing and being more enriched in A towards the outer edges. The overall composition is equivalent to the original composition of the liquid mixture N.

Zoning of this type is a typical feature of the plagioclase feldspars where albite ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$) and anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) are the extreme end members of a solid solution series. It is also found in the olivine, pyroxene and melilite series. In every case the 'core' of zoned crystals is richer in the component of higher melting point.

The system illustrated in Fig. X.8, is the simple case of two components which are completely miscible in the solid and liquid states. Other cases are known where a maximum or minimum point occurs in the diagram as shown in Figs. X.9A and B. These maxima or minima are of interest because they are examples of invariant points where apparently the Phase Rule does not so predict. At the points M in both diagrams, only two phases can co-exist, namely a homogeneous liquid phase and a solid phase of identical composition with complete miscibility of the components. Hence, with $P = 2$ and $F = 1$, the points are theoretically *univariant*.

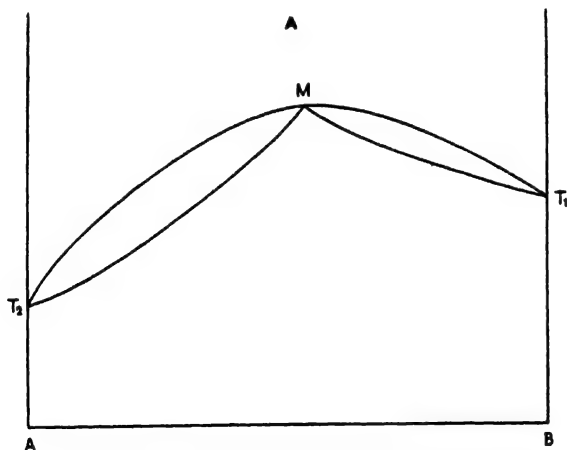


FIG. X.9A. THE PHASE DIAGRAM OF MISCIBLE COMPONENTS WITH A MAXIMUM POINT

A concise explanation of this apparent anomaly is outside the scope of this volume—it arises as a result of an over-simplification of the Phase equation. Terms which appear in the original form cancel out in the vast majority of systems, but in

this one case they have to be considered and contribute to the equation to make the maximum and minimum points invariant.

Examples of a maximum-point diagram (Fig. X.9A) are not common in ceramic systems, but they are the usual form of constant melting or boiling point systems, such as alcohol and water. There are, however, some important mineral systems with a minimum point, and the iron-calcium monticellite $2(\text{CaO}, \text{FeO})\text{SiO}_2$ is an example.

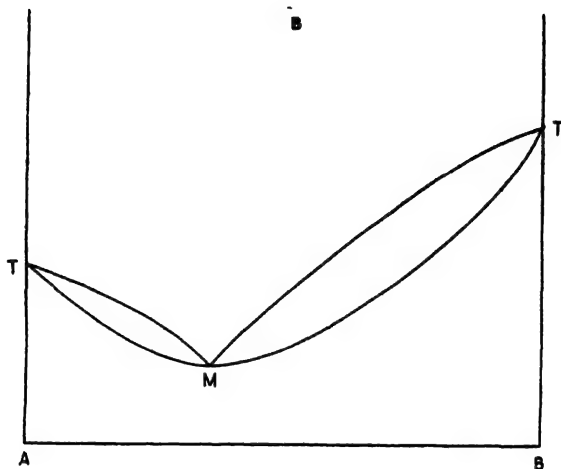


FIG. X.9B. THE PHASE DIAGRAM OF MISCIBLE COMPONENTS WITH A MINIMUM POINT

Partial miscibility in the solid state is of common occurrence in silicate systems. Many components will mix together to form a completely miscible liquid but a homogeneous, solid, crystalline solution is produced over only a limited range of compositions.

The simplest type is illustrated in Fig. X.10 where the two components form a eutectic mixture. Limited solid solution formation is encountered in mixtures rich in either component, but intermediate mixtures do not form a homogeneous solid phase.

The addition of component A to component B causes a reduction in the melting point of the latter and, similarly, additions of B to A also produce a lowering. When a melt of any particular composition is cooled, crystallisation will begin at the temperature of the liquidus line in that region. The composition of the first solid phase to form is given by drawing a horizontal tie-line (p. 551) to cut the solidus line. The composition of the liquid phase follows the phase boundary line and, ideally, the solid solution changes in composition progressively. This process will continue until all liquid disappears when one solid homogeneous phase will be the result or until the liquid reaches the composition of the eutectic mixture E. At this point liquid can be in equilibrium with two solid solutions of composition M and N. True invariant conditions exist and the two solid phases are distinctly separate.

Any mixture with a composition between the points M and N will solidify to give two separate crystalline solutions. Mixtures richer in component A than the point M or richer in B than is mixture N will finally crystallise as one homogeneous solid solution phase, provided equilibrium cooling has taken place. The composition of this single phase will be that of the original mixture.

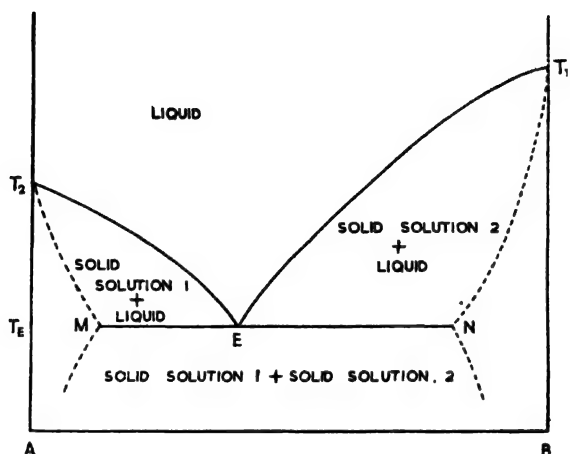


FIG. X.10. THE PHASE DIAGRAM OF TWO COMPONENTS WITH PARTIAL SOLID SOLUTION

Solid solutions may also be associated with both stable and incongruent compound formation. The establishment of the amount of solid solution in silicate systems is difficult and it is only in recent years that exhaustive studies using specialised techniques have established their existence.

Polymorphic Changes in Binary Systems. The changes described in the various two component systems may be further complicated by the presence of inversion or conversion phenomena, where a crystalline entity changes into another modification. Many minerals are known which are polymorphic or are capable of existing in more than one form. Silica is perhaps the best known example; three well-defined minerals are known, each of which has separate characteristic inversive phenomena (p. 162).

When changes of this type take place below the lowest temperature at which liquid may exist and, where there is no interaction or miscibility between the two components of a binary system, the polymorphic transformation will proceed at a definite temperature, which is independent of the composition of the mixture. Beyond the introduction of a horizontal line at the appropriate temperature (T_3) in the solidus region, the equilibrium diagram in such cases is unchanged (Fig. X.11A).

When a transformation occurs above the eutectic temperature an inflection point usually appears in the diagram as in Fig. X.11B. This is to be expected as the latent heat of fusion of the two forms will most probably be different. In Fig. X.11B, the polymorphic change takes place in component A at a temperature of T_4 . Such

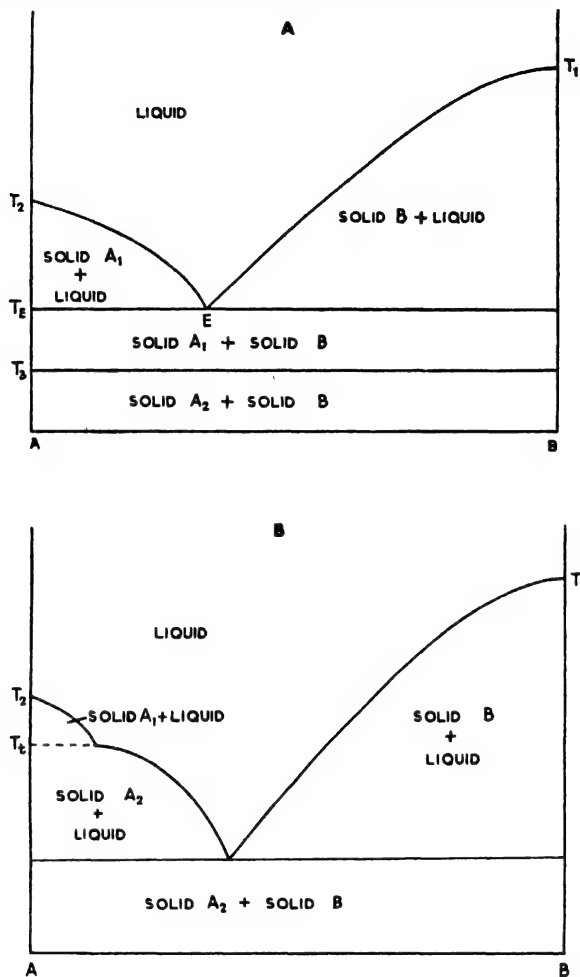


FIG. X.11. THE PHASE DIAGRAM OF A BINARY MIXTURE IN WHICH ONE COMPONENT UNDERGOES A POLYMORPHIC CHANGE

A below and B above the eutectic temperature

a diagram represents the equilibrium conditions of mixtures of silica and alkaline oxides where cristobalite, tridymite and quartz may all have stability ranges in certain regions of composition and temperature.

Examples are common in silicate systems, in which an unstable crystalline phase may separate from a liquid melt on cooling. In such cases, the equilibrium diagram will be different from that where the stable phase is produced. If two components form a eutectic mixture, but one component can be present as either a stable and unstable variety, the eutectic temperature of the mixture containing the stable

form will be higher than that of the unstable modification as shown in Fig. X.12. This rule was first defined by Tamman and it applies also to the fusion and solubility relationships. The unstable form is always more reactive and has a lower melting point than the stable form. Thus quartz can be melted if it is very pure at 1670°C . without prior conversion to the stable phase (cristobalite) which has a melting point of 1720°C .

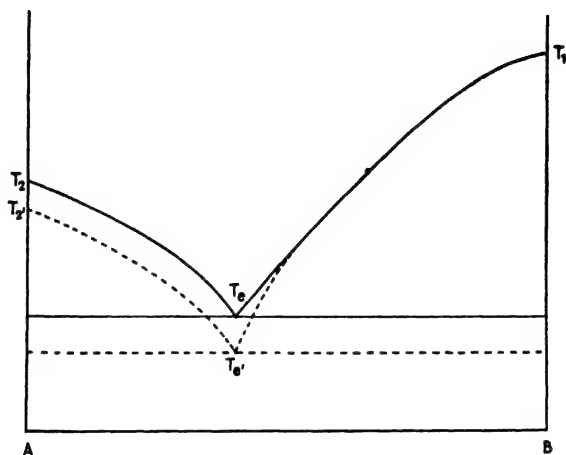


FIG. X.12. THE CHANGE IN THE PHASE DIAGRAM WHEN ONE COMPONENT CAN EXIST IN A STABLE AND AN UNSTABLE FORM

The crystallisation of an unstable phase may suppress certain characteristics of the equilibrium diagram of stable components. Kracek, Bowen and Morey¹ describe such a condition in the system $\text{K}_2\text{O}/\text{SiO}_2$. Towards the silica-rich end of the diagram, mixtures are completely liquid at temperatures within the stability range of quartz. If this stable phase can be crystallised, a stable compound $\text{K}_2\text{O} \cdot 4\text{SiO}_2$ will also form within the composition range as indicated by Fig. X.13. However, equilibrium is reached so sluggishly that quartz cannot normally be crystallised even though the temperature is below 870°C .; instead tridymite or cristobalite crystallise from the melt. Under these conditions, the crystal phase $\text{K}_2\text{O} \cdot 4\text{SiO}_2$ does not appear and a low-temperature eutectic with the silica phase and $\text{K}_2\text{O} \cdot 2\text{SiO}_2$ may be observed.

Polymorphous changes in solid solution. The transformation of a pure mineral into a polymorphic variety invariably takes place at a definite temperature although such changes are sometimes very sluggish. When solid solution occurs, however, an inversion-interval may replace the invariant point and the change or changes take place at temperatures removed from those in the pure material.

Miscibility in the solid state is most likely when the components are similar in crystalline form. When polymorphic changes in crystal structure take place in one component of such a mixture, the ratio of the two components which can take part in

¹ Kracek, F. C., Bowen, N. L. and Morey, G. W., *J. Phys. Chem.*, **41**, 1188, 1937.

the high temperature solid solution will probably be different from that in the original mixture. Furthermore, the formation of solid solutions usually results in an alteration of the temperature of inversion in a comparable way to the change in the melting or boiling point produced by mixing components. Solid phase relationships in the region of polymorphic changes are complex but can be represented by characteristic equilibrium diagrams.

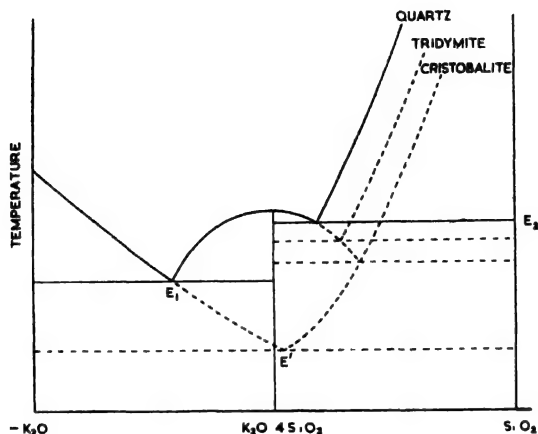


FIG. X.13. THE PARTIAL PHASE DIAGRAM OF THE K_2O/SiO_2 SYSTEM (after Kracek, Bowen and Morey)

Polymorphic inversions in systems with solid solution are commonly found in silicate mixtures, but the importance of these changes and the way in which they are influenced by other components has only been recognised in recent years. The invariable result of introducing a component capable of forming solid solutions with a polymorphic material is to alter the temperature at which inversions take place. As in the case of the melting of a binary solid solution, a heterogeneous field is present, bounded by two phase-boundary lines. The upper line represents the transformation of a high to a low form in the presence of varying amounts of the second miscible component, whilst the lower phase-boundary curve indicates the variation in the low to high transformation with the degree of solid solution. At any one particular temperature, therefore, a solid solution of the high temperature modification of an inverting mineral can be in equilibrium with a solid solution of the low temperature form. The inversion effect thus takes place over a temperature interval and not at one specific point.

There are two well-established cases covered by Konow's Rules which state:

If the low temperature or α -phase of the inverting material contains *less* of the additional miscible component than the high or β -form, the inversion temperature of the resulting solid solution will be *lower* than that of the pure mineral.

Conversely, if the high, or β -variety is *less rich* in the other component than the low form, the inversion temperature in the solid solution will be *raised* with respect to that of the pure mineral.

These two cases are shown in Fig. X.14, the former case being on the left-hand side of the diagram, whilst the latter is on the right. Changes of this type are frequently interposed on already familiar diagrams such as the two illustrated in Fig. X.15A and B. The diagrams are of two components with partial miscibility in the solid state, where one component (A in both cases) has an inversion effect. Fig. X.15A is commonly encountered in metallurgical studies, whilst Fig. X.15B is often associated with silicate systems. Nephelite, for example, inverts to carnegieite at 1254° C., but when a plagioclase feldspar such as albite or anorthite enters into solid solution with it, the temperature of the transformation is increased (see Fig. X.30).

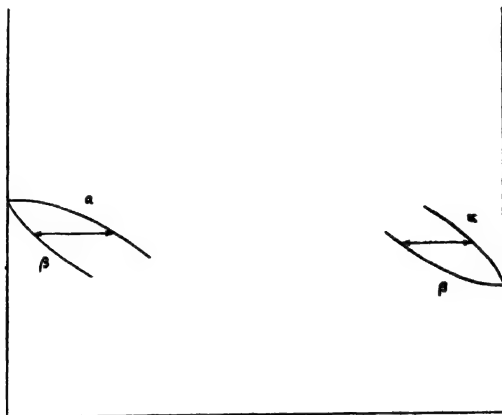


FIG. X.14. THE EFFECT OF POLYMORPHIC CHANGES ON THE PHASE RELATIONSHIPS IN A BINARY SOLID SOLUTION

The close similarity of the inversion effect in cristobalite to the example just cited, suggests that the well-known variation in temperature of the transformation of the α - to the β -variety of this mineral, may be due to solid solution effects. The crystal structure of cristobalite is sufficiently open to contain cations such as Ca^{2+} , Mg^{2+} , Na^{+} . Furthermore, Barth, Hummel and other workers have shown that silicon atoms in the structure can be replaced by aluminium with the inclusion of electrical-balancing cations without changing the atomic arrangement. Evidence which favours this theory is that the inversion of cristobalite is at a higher temperature when the sample has been subjected to prolonged or high temperature heat treatment. This would also have the effect of increasing the amount of solid solution which in turn should increase the inversion temperature, provided the equilibrium diagram is of the form indicated in Fig. X.15B.

The solid solution theory of the cristobalite inversion effect is difficult to establish with certainty. Solid solution within the cristobalite lattice cannot be confirmed by X-rays when the amounts of substituted atoms are small and randomly situated. It has, however, been clearly demonstrated (by thermal and microscopic evidence) that cristobalite with an apparently high inversion-temperature transforms over a range or interval and not at one specific temperature.

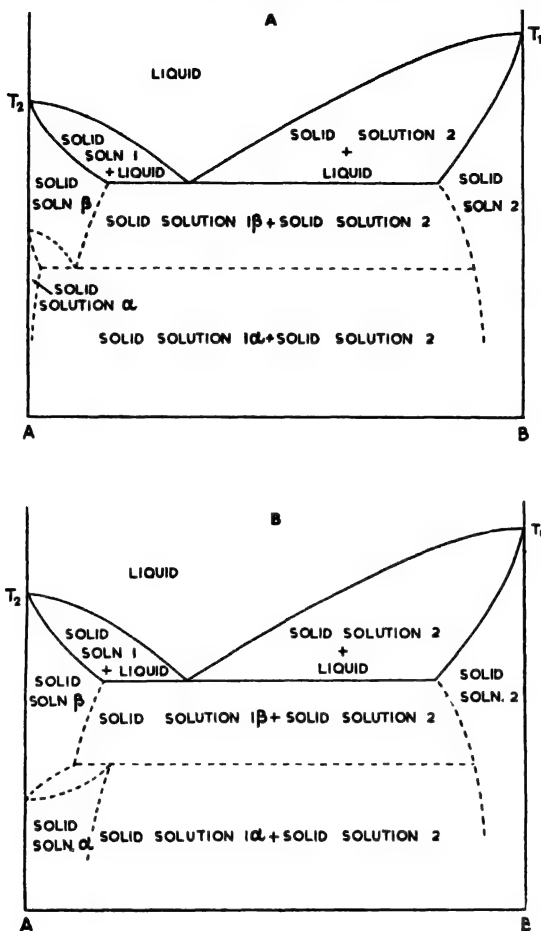


FIG. X.15. EXAMPLES OF SOLID SOLUTION WITH A POLYMORPHIC CHANGE IN BINARY MIXTURES

Partial Miscibility in the Liquid Phase. In almost all the theoretical cases considered so far, the assumption has been made that the liquid phase is homogeneous and the two components are miscible in all proportions. Examples are not common of components which are completely immiscible in the liquid state, but many binary systems have partial fields of composition where the two components exist as independent liquid phases.

Fig. X.16 illustrates a case where, within a narrow field of composition bounded by M and N and a temperature between T_3 and T_4 , two liquids have independent existence. A mixture of composition C will form a homogeneous liquid at a temperature above T_3 . When cooled to the temperature of the point O, however, two liquid phases separate. As cooling proceeds further, the composition and relative

amounts of the two liquid phases alter. If a horizontal line is drawn to cut the isopleth (line of constant composition C), then the compositions of the liquid phases at that temperature are given by the intercepts on the phase boundary curve. At the temperature of the point C_1 , for example, the two liquid compositions are given by the points P and Q and the relative amounts of each at that temperature may be calculated by the lever principle around C_1 (p. 546).

$$\frac{\text{Amount of liquid of composition } P}{\text{Amount of liquid of composition } Q} = \frac{QC_1}{C_1P}$$

Partial immiscibility phenomena are often encountered in the silica-rich region of alkaline earth silicate systems.

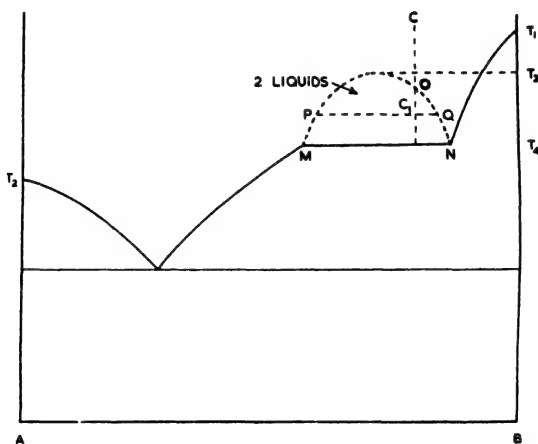


FIG. X.16. THE PHASE DIAGRAM OF A BINARY MIXTURE WITH LIQUID MISCIBILITY OVER ONLY A LIMITED FIELD OF COMPOSITION

Binary Systems in Ceramic Materials. There are many binary systems of importance to ceramists, and almost all the phase equilibrium conditions described previously are to be found.

The *alumina/silica* diagram is perhaps the most commonly encountered binary system. Seger, in 1893, was the first to attempt its construction by noting the temperature at which a liquid phase appeared in mixtures of different composition. Bowen and Greig¹ studied the system in more detail and deduced the phase diagram shown in Fig. X.17 in which the salient features include a eutectic point at a temperature of 1545° C. at a composition of 5.5 per cent alumina, 94.5 per cent silica. A peritectic point at 1810° C. indicates that a compound is formed which is not stable to its melting point. This is the well-known mineral, mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) which is produced by heating almost all alumino-silicate mixtures and which at 1810° dissociates into corundum ($\alpha\text{-Al}_2\text{O}_3$) and a liquid phase.

¹ Bowen, N. L. and Greig, J. W., *J. Amer. Ceram. Soc.*, 7, 242, 1924.

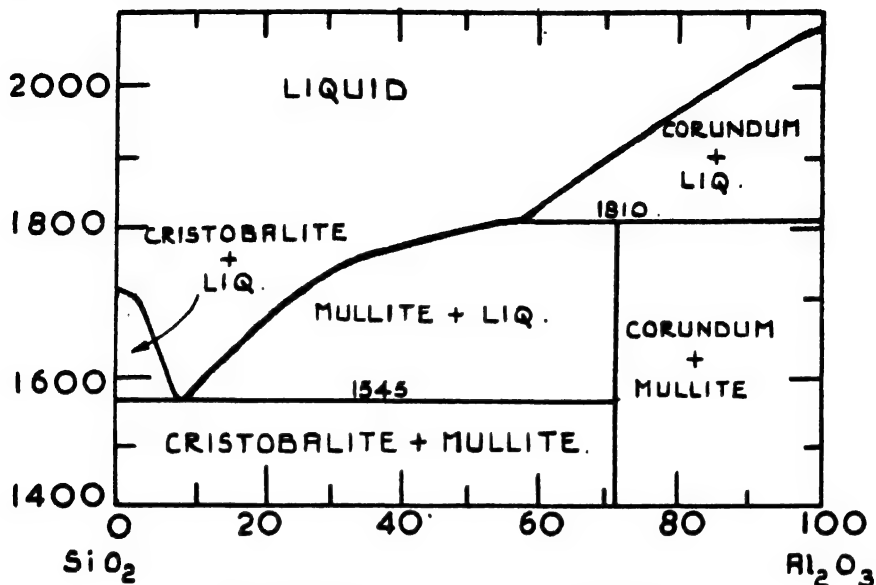


FIG. X.17. THE ALUMINA/SILICA PHASE DIAGRAM
(modified after Seger)

The *lime-silica* system has been examined in detail by Ranken and Wright¹ and modified by Greig.² There are three eutectic points as follows:

1. At a temperature of 1436° C. a eutectic mixture consisting of tridymite and pseudo-wollastonite is formed.
2. At 1455° C. a eutectic containing 53 per cent of lime and 47 per cent of silica consisting of pseudo-wollastonite and $3\text{CaO} \cdot 2\text{SiO}_2$ is formed.
3. At 2065° C. a eutectic containing 67.5 per cent of lime and 32.5 per cent of silica and consisting of calcium orthosilicate and lime is formed.

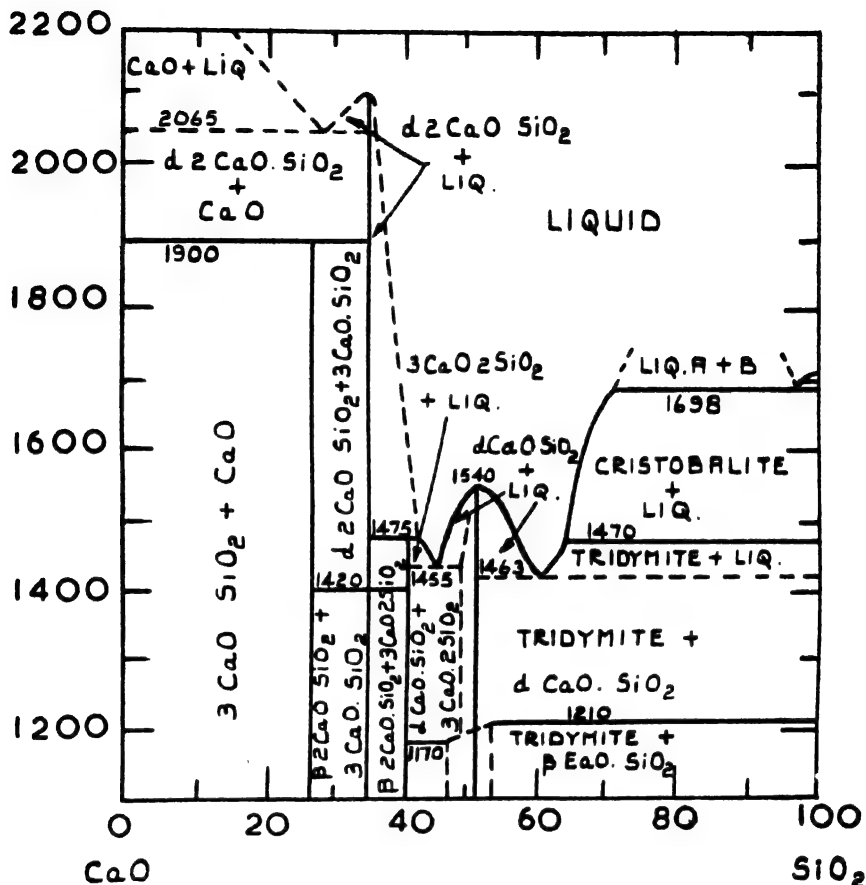
Four definite binary compounds are shown in the equilibrium diagram (Fig. X.18), namely, calcium orthosilicate ($2\text{CaO} \cdot \text{SiO}_2$) which melts at 2130° C., calcium metasilicate ($\text{CaO} \cdot \text{SiO}_2$) which melts at 1540° C. (J. Cobb found that the orthosilicate is formed unless there is a large excess of silica present, in which case the metasilicate may be formed); a compound with the formula $3\text{CaO} \cdot 2\text{SiO}_2$, which melts incongruently at 1475° C.; and tricalcium silicate, $3\text{CaO} \cdot \text{SiO}_2$, which dissociates into CaO and $2\text{CaO} \cdot \text{SiO}_2$ at 1900° C. which is below the eutectic temperature (2065° C.).

Calcium orthosilicate exists in three forms:

- α Stable above 1410° C.—monoclinic; specific gravity 3.27; hardness, 5–6.
- β Stable 1410° C.–675° C.—orthorhombic; specific gravity 3.28.
- γ Stable below 675° C.—monoclinic; specific gravity 2.97.

¹ Ranken, G. A. and Wright, F. E., *Amer. J. Sci.*, 39, 5, 1915.

² Greig, J. W., *Amer. J. Sci.*, 13, 1, 1927.



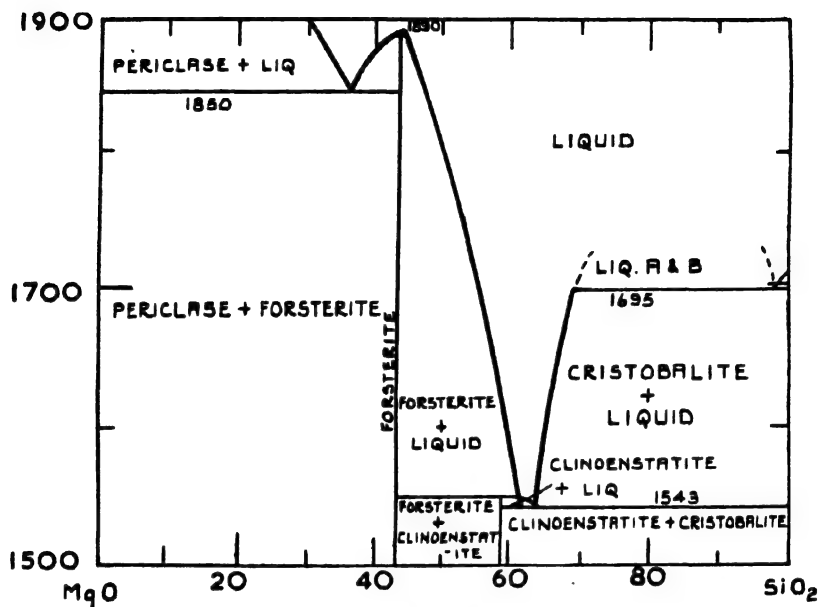


FIG. X.19. THE MAGNESIA/SILICA PHASE DIAGRAM
(after Bowen and Anderson)

- Four Compounds: (a) 2BaOSiO_2 (melting point 1850°C . (approx.)).
 (b) BaOSiO_2 (melting point 1604°C .).
 (c) $2\text{BaO}_3\text{SiO}_2$ (melting point 1450°C .).
 (d) BaO_2SiO_2 (melting point 1426°C .).

Three Eutectics, as shown in Table X.I.

TABLE X—I. THE EUTECTICS IN THE
 $\text{BaO}-\text{SiO}_2$ SYSTEM

	Barium oxide per cent	Silica per cent	Melting point
(a)	47.0	53.0	1374°C .
(b)	65.0	35.0	1435°C .
(c)	74.5	25.5	1551°C .

In addition to the foregoing, mixtures of $2\text{BaO}_3\text{SiO}_2$ and BaO_2SiO_2 form a continuous series of solids containing these components in any proportions.

The *strontia-silica* system includes, according to P. Eskola,¹ the following compounds and eutectics:

¹ Eskola, P., *Amer. J. Sci.*, 4, 345, 1922.

Two *Compounds*: (a) 2SrOSiO_2 (melting point above range of electric furnace—about $1800^\circ\text{C}.$).

(b) SrOSiO_2 (melting point $1578^\circ\text{C}.$).

Two *Eutectics*, as shown in Table X.II.

TABLE X—II. THE EUTECTICS IN THE
 SrO—SiO_2 SYSTEM

	<i>Strontia per cent</i>	<i>Silica per cent</i>	<i>Melting point</i>
(a)	46.5	53.5	$1385^\circ\text{C}.$
(b)	65.5	34.5	$1545^\circ\text{C}.$

It is of interest to note that with the exception of barium oxide, all alkaline earth oxide-silica systems have a range in the silica-rich part of the diagram where the two components form immiscible liquids. This is of importance in basic open hearth practice, where silica bricks are used as roof bricks. The dusts rich in free lime are not exceptionally corrosive if the silica is of high purity because there is little tendency to mix. Should a third component, such as alumina, be present, even in small amounts, this desirable feature is destroyed and complete homogeneity in the liquid phase develops. The slagging action of the lime on the refractory is then greatly enhanced.

The *zinc oxide-silica system* includes only one definite compound (willemite Zn_2SiO_4 , melting point $1512 \pm 3^\circ\text{C}.$), and two eutectics:

One melting at $1432^\circ\text{C}.$ containing 49.1 mol. per cent $\text{ZnO}.$

One melting at $1507^\circ\text{C}.$ containing 77.5 mol. per cent $\text{ZnO}.$

No evidence of the metasilicate ($\text{ZnO}.\text{SiO}_2$, melting point $1437^\circ\text{C}.$) found by Jaeger and Van Klooster was obtained by Bunting.¹

The *manganese oxide-silica system*. Manganese oxide and silica produce orthosilicates and metasilicates:

2MnOSiO_2 (melting point $1290\text{--}1300^\circ\text{C}.$) is identical with the mineral *tephroite*. Artificial tephroite has no definite melting point, but darkens on heating and decomposes before melting completely.

MnOSiO_2 (melting point $1273^\circ \pm 1^\circ\text{C}.$) is identical with the mineral *rhodonite* which melts between 1221° and $1270^\circ\text{C}.$ Both these minerals, according to White, Howat and Hay,² decompose before melting, giving peritectic points (see Fig. X.6).

The *iron oxide-silica systems* are complicated by the existence of three iron oxides and by the comparative ease with which the red ferric and the black magnetic oxides can be reduced to form the dark ferrous oxide. At temperatures in excess of about $1000^\circ\text{C}.$, however, all forms convert more or less readily into *wustite*, FeO , and Bowen and Schairer³ have deduced the relationships between this component and silica as shown in Fig. X.20.

¹ Bunting, E. N., *Bur. Stand. J. Res.*, **4**, 134, 1930.

² White, J., Howat, D. D. and Hay, R., *J. Roy. Tech. Coll. (Glasgow)*, **3**, 239, 1933–36.

³ Bowen, N. L. and Schairer, J. F., *Amer. J. Sci.*, **24**, 200, 1932.

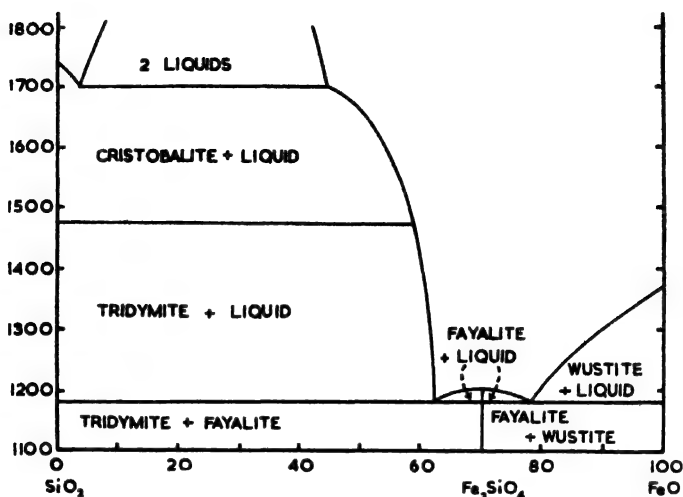


FIG. X.20. THE IRON OXIDE/SILICA PHASE DIAGRAM
(after Bowen and Schairer)

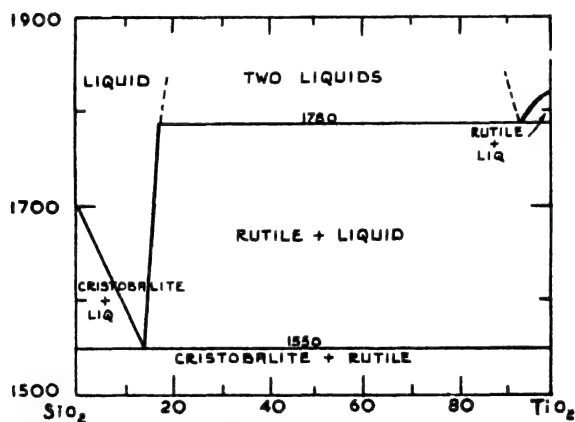


FIG. X.21. THE TITANIA/SILICA PHASE DIAGRAM
(after De Vries, Roy and Osborn)

One compound, *fayalite*, Fe_2SiO_4 , has been found and there are eutectic points at 1183°C . and 1181°C . containing 62 per cent and 77 per cent FeO respectively. Two immiscible liquid phases form in the silica-rich region in a similar way to alkaline earth-silica mixtures.

The *titania-silica* system was studied by DeVries, Roy and Osborn;¹ they found

¹ DeVries, R. C., Roy, R. and Osborn, E. F., *Trans. Brit. Ceram. Soc.*, 53, 525, 1954.

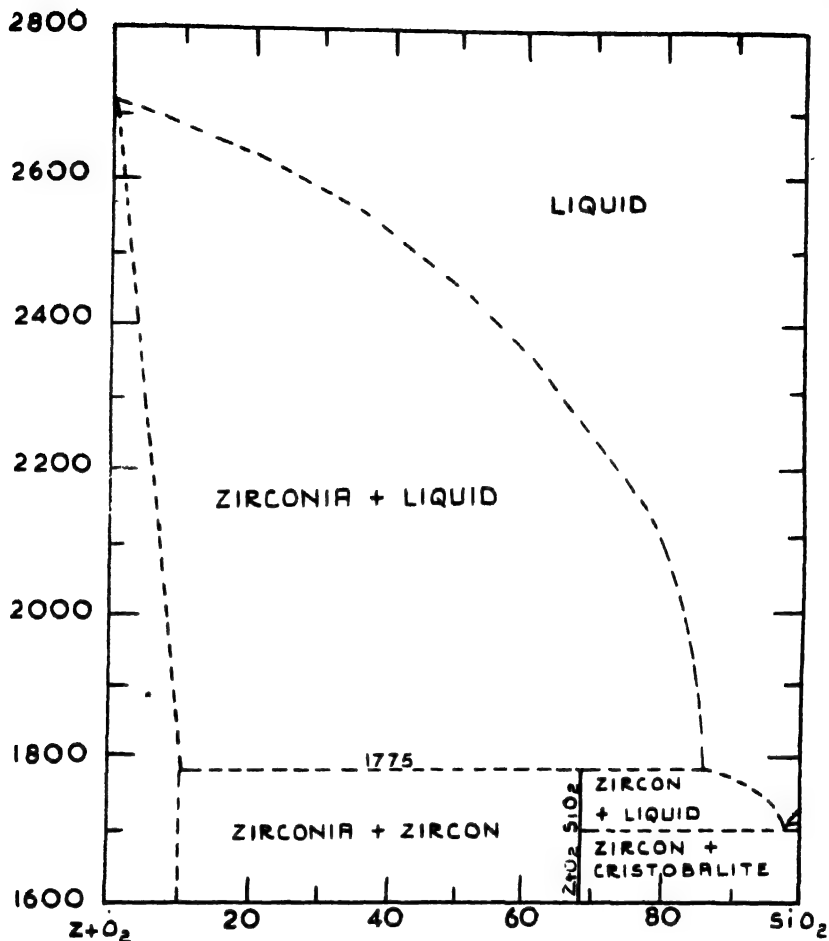


FIG. X.22. THE ZIRCONIA/SILICA PHASE DIAGRAM
(after Geller and Yavorsky)

only one eutectic point at 1550° C., but showed that titania and silica were immiscible in the liquid form over most of the composition range. The phase diagram is shown in Fig. X.21.

The *zirconia-silica* system has been investigated by Geller and Yavorsky,¹ and as Fig. X.22 shows, contains the compound $ZrSiO_4$, zircon, which melts incongruently and gives rise to a peritectic point at 1775° C. The eutectic at a little below 1700° C. contains only about 1 per cent ZrO_2 .

The *alkali oxide-silica* mixtures give complex diagrams, characterised by many compounds and extremely low melting point eutectics. The principal features of

¹ Geller, R. F. and Yavorsky, P. J., *J. Res. Nat. Bur. Stand.*, 35, 109, 1945.

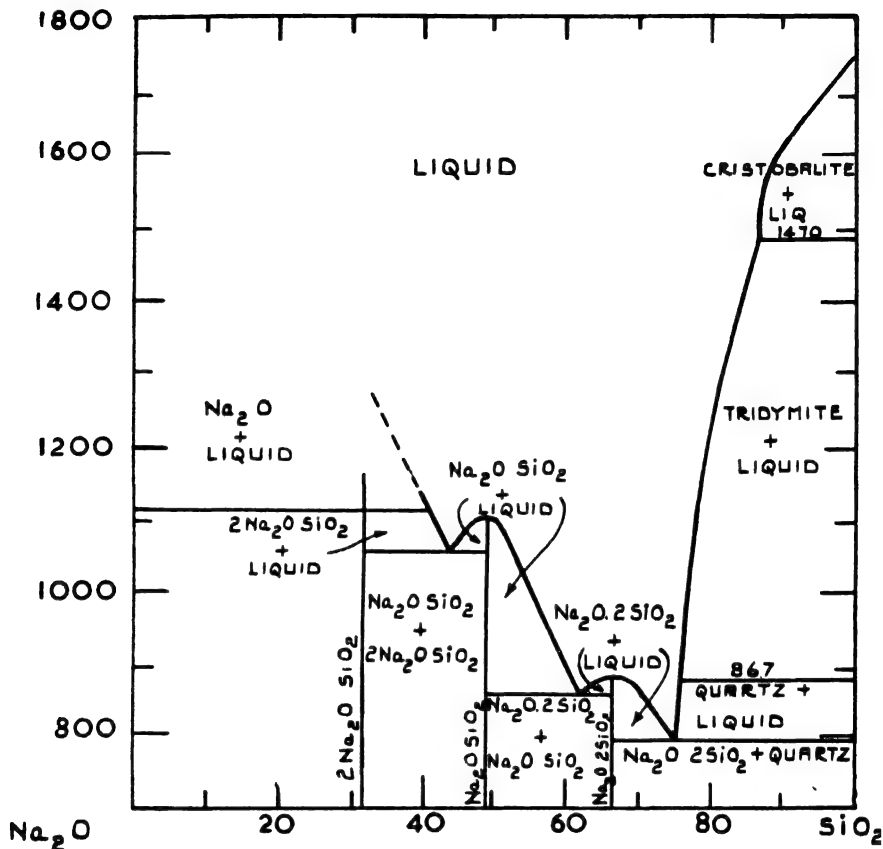


FIG. X.23. THE SODIUM OXIDE/SILICA PHASE DIAGRAM
(after Kracek)

the Li_2O , Na_2O , K_2O —silica systems are summarised in Table X.III, and the phase diagram of soda/silica in Fig. X.23.

Much interesting information can be derived from a comparison of the various binary systems with silica as one component. The amount of liquid formed as the temperature is raised when a small amount of impurity is present in silica may be predicted.

If 1 per cent molar concentration of the various oxides is mixed with pure silica, a liquid will first form at the appropriate eutectic point and its amount is given by applying the lever principle around the composition point (see p. 546). The amount of liquid at all temperatures above the eutectic may be similarly assessed until the liquidus line is reached, when no solid matter remains.

Fig. X.24 shows the amount of liquid forming as the temperature is raised with several 1 per cent oxide-silica mixtures. It is significant that although with alumina, liquid does not form until 1545°C ., the amount present at 1650°C . is in excess of

TABLE X—III. CHARACTERISTIC FEATURES OF ALKALI OXIDE-SILICA SYSTEMS

<i>Alkali Oxide</i>	<i>Compounds</i>			<i>Eutectics</i>		
	Formulae M. pt. °C.	$\text{Li}_2\text{Si}_2\text{O}_5$ Incong.	Li_2SiO_3 1201	Li_4SiO_4 Incong.	Li_2O Temp. °C.	55% 1024
Li_2O	—	—	—	—	—	—
Na_2O	Formulae M. pt. °C.	$\text{Na}_2\text{Si}_2\text{O}_5$ 874	Na_2SiO_3 1080	Na_4SiO_4 Incong.	Na_2O Temp. °C.	24% 730
						37% 840
K_2O	Formulae M. pt. °C.	$\text{K}_2\text{Si}_2\text{O}_5$ 1045	K_2SiO_3 976	—	K_2O Temp. °C.	26.4% 767
						32.4% 742
						45.0% 780
						—

that in the sodium oxide-silica mixture. For this reason, alumina is an undesirable impurity in the raw materials for the manufacture of silica bricks.

The *lime-alumina system* includes various calcium aluminates which are much more fusible than either lime or alumina.

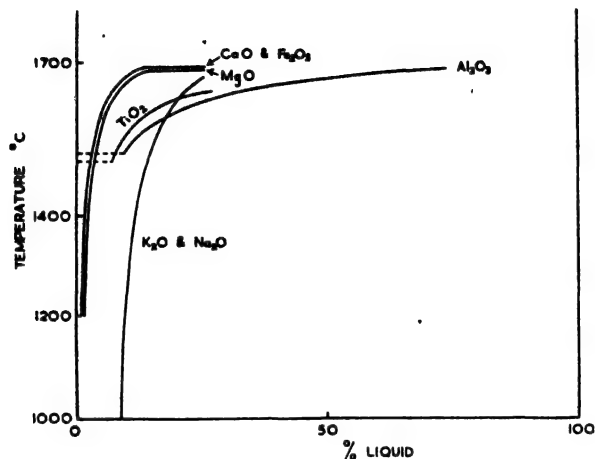


FIG. X.24. THE AMOUNT OF LIQUID FORMED WITH MIXTURES OF SILICA WITH 1 PER CENT OF VARIOUS OXIDES AT DIFFERENT TEMPERATURES

Free lime and alumina begin to interact between 800° C. and 900° C.; the reaction becomes very rapid as 1100° C. is approached and, according to Cobb, is practically complete at 1300° C. The chief calcium aluminates which are found in this system are:

- (a) $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ (melting point 1455° C.),
- (b) $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ (dissociating at 1530° C.),
- (c) $\text{CaO} \cdot \text{Al}_2\text{O}_3$ (melting point 1600° C.),
- (d) $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$ (melting point 1720° C.).

Both $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ and $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$ have stable and unstable forms. There are three eutectics, shown in Table X.IV.

TABLE X—IV

Eutectics	Lime per cent	Alumina per cent	Melting point
(a)	47	53	1400° C.
(b)	33.5	66.5	1590° C.
(c)	24	76	1700° C.

They are not found in burned clays. $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ may be formed at temperatures below 1100° C., but above this temperature a compound richer in alumina is found

which is insoluble in hydrochloric acid in the cold, whilst the more calcareous compound is completely soluble. The phase diagram of alumina and lime is shown in Fig. X.25 due to Rankin and Wright.¹

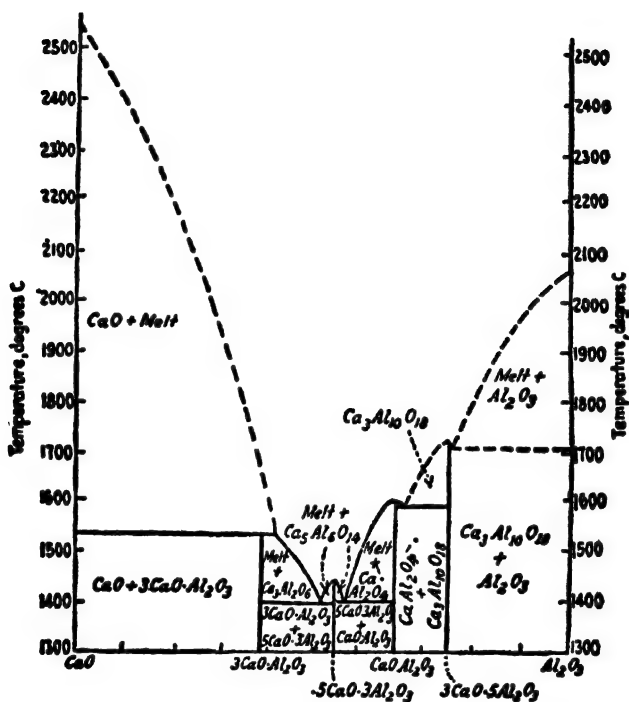


FIG. X.25. CONCENTRATION/TEMPERATURE DIAGRAM OF THE LIME-ALUMINA SYSTEM

The *magnesia-alumina system*² yields one compound—spinel ($\text{MgO} \cdot \text{Al}_2\text{O}_3$), with a melting point of 2135°C . and the three eutectics shown in Table X.V.

TABLE X—V

Constituents	Magnesia per cent	Alumina per cent	Melting point
Spinel/magnesia	45	55	2030°C .
Spinel/ α -alumina	98	2	$1925 \pm 40^\circ \text{C}$.
Spinel/ β -alumina	92	8	$1925 \pm 40^\circ \text{C}$.

Spinel forms a series of solid solutions with α -alumina. The phase diagram is shown in Fig. X.26.

¹ Rankin, G. A., and Wright, F. E., *Amer. J. Sci.*, 39, 11, 1915.

² Rankin, G. A., and Merwin, H. E., *Amer. J. Sci.*, 45, 304, 1918.

The *lime-magnesia system*¹ contains one eutectic composed of 67 per cent of lime and 33 per cent of magnesia; it melts at 2300° C. (see Fig. X.27). Tröjer and Konopicky² have suggested that partial solid solution of magnesia in lime takes place. Up to 3 per cent of magnesium oxide may be present in calcium oxide which modifies the equilibrium diagram of lime-rich mixtures to the form shown in Fig. X.10.

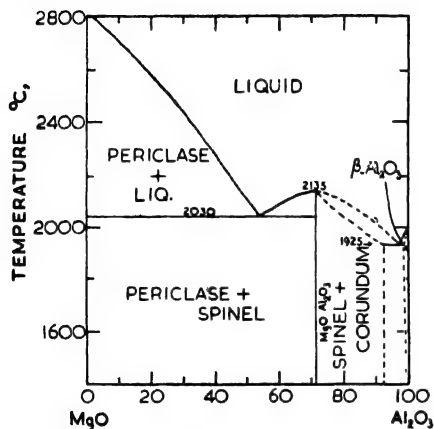


FIG. X.26. PHASE DIAGRAM OF THE MAGNESIA-ALUMINA SYSTEM

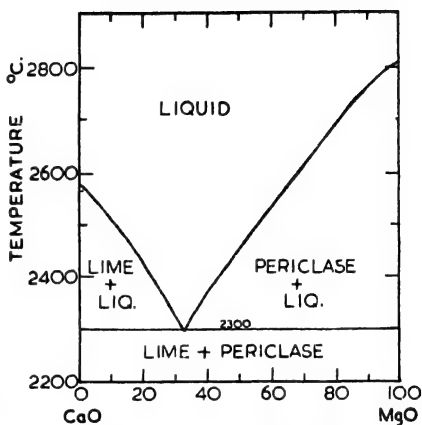


FIG. X.27. TEMPERATURE/CONCENTRATION DIAGRAM OF THE LIME-MAGNESIA SYSTEM

The *iron oxide-alumina system* like the corresponding silica system is complicated by the existence of three iron oxides (p. 565). So far as the ferrous oxide-alumina system is concerned the chief compound is *hercynite* (FeOAl_2O_3). The iron oxide-alumina system has not, however, been fully investigated.

The *iron oxide-lime system*³ is complicated like the corresponding ones containing alumina and silica respectively. When lime and iron oxide are heated together ferrates may be formed. The two chief compounds are calcium metaferrate (CaOFe_2O_3), which melts at 1215° C., and dissociates at the same temperature, forming long, black, needle-shaped crystals, whilst the second compound calcium orthoferrate ($2\text{CaOFe}_2\text{O}_3$) melts at 1436° C. and almost immediately dissociates, forming black crystals having a yellowish-brown tinge by reflected light. The eutectic contains 8 per cent of lime and 92 per cent of ferric oxide; it melts at 1203° C. The phase diagram, due to Sosman,⁴ is shown in Fig. X.28.

Very little calcium meta- or ortho-ferrate is formed when clays are burned as the proportion of iron oxide is not usually sufficient.

The *iron oxide-magnesia system* has been investigated by Roberts and Merwin⁵ who found only one compound ($\text{MgO} \cdot \text{Fe}_2\text{O}_3$) which dissociates on heating.

¹ Rankin, L. G. A. and Merwin, H. E., *J. Amer. Chem. Soc.*, 38, 571, 1916.

² Tröjer, F. and Konopicky, K., *Radex-Rundschau*, 4, 161, 1949.

³ Sosman, R. B. and Merwin, H. E., *J. Wash. Acad. Sci.*, 6, 532, 1916.

⁴ Amer. *J. Sci.*, 39, 11, 1915.

⁵ Paper 732, *Geophys. Labor., Carnegie Inst. (Washington, U.S.A., 1931)*.

Ferrous oxide enters into solid solution in magnesia to a limited extent and ferric oxide may combine with magnesia to form magnesioferrite (MgOFe_2O_3). This substance also forms mixed crystals with magnesia. It has been detected in magnesia bricks by Cornu and Cronshaw independently.

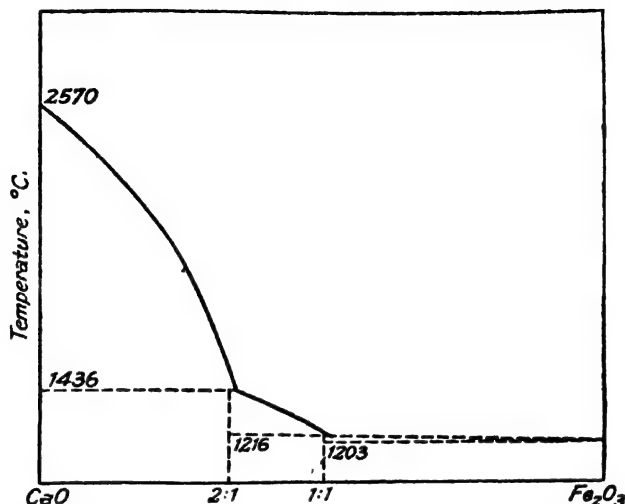


FIG. X.28. PHASE DIAGRAM OF THE LIME-FERRIC OXIDE SYSTEM (Sosman)

Both ferric and ferrous oxide sometimes react rapidly with magnesia. For this reason magnesia bricks should not usually be heated in contact with very hot iron oxide. In what are known as 'Metalkase bricks', which are iron cylinders packed with dead-burned magnesia, use is made of the reaction of these two substances to form a magnesian mass with a very strong bond.

Binary Systems of Complex Components. Although it is most usual to consider equilibrium diagrams in terms of the simplest components (namely oxides), it is frequently convenient to select complex compounds for this purpose. A small region of a ternary or multi-component system can be more clearly appreciated by constructing the binary field between two compounds which are formed in the mixture; in fact, a ternary equilibrium diagram is frequently built up from information given by firing mixtures of two compounds in definite proportions.

A simple example of the use of complex components is shown in Fig. X.29 where the phase relationships between sodium disilicate ($\text{Na}_2\text{O} \cdot 2\text{SiO}_2$) and corundum (Al_2O_3) in the ternary system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ are illustrated. The comparatively simple binary diagram shows congruent compound formation of the mineral carnegieite $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ which transforms to nephelite at 1254°C . Binary eutectics are formed at 768°C . and 1475°C .

Another example from the same ternary mixture but where two complex compounds are taken as components is shown in Fig. X.30. If carnegieite (or nephelite) $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ and the sodium felspar, albite, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ are regarded

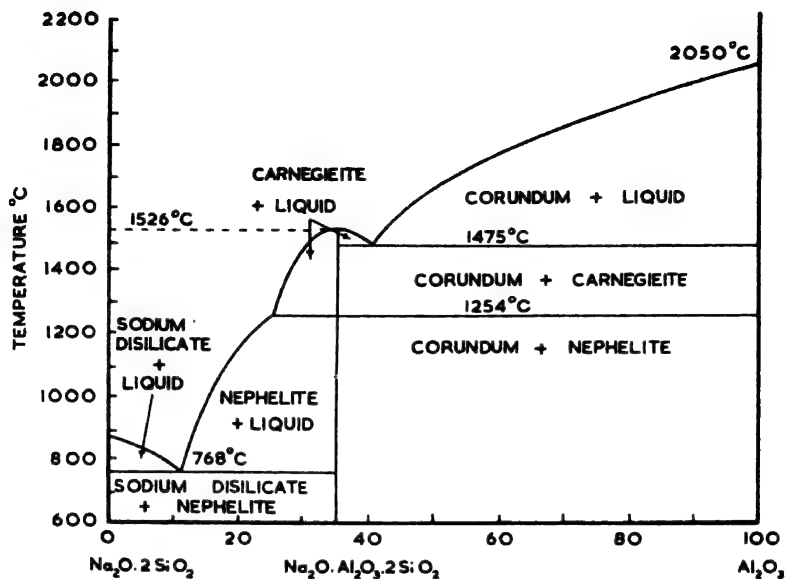


FIG. X.29. THE PHASE RELATIONSHIPS BETWEEN SODIUM DISILICATE AND CORUNDUM

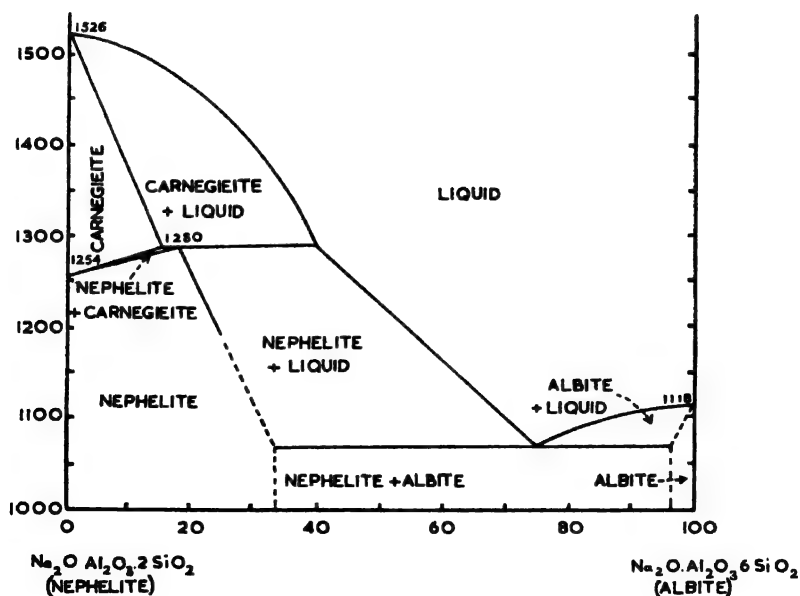


FIG. X.30. THE PHASE RELATIONSHIPS BETWEEN CARNEGIEITE AND ALBITE

as the components of a binary mixture, the phase relationships indicate binary eutectic formation at 1068° C. There is also partial solid solution of albite in nephelite and nephelite in albite (see Fig. X.10) and this changes the temperature of inversion of the carnegieite to nephelite transformation.

There are many other binary systems of importance in ceramic studies, some of which have been collected by Levin, McMurdie and Hall and have been published by the American Ceramic Society.¹

THREE-COMPONENT OR TERNARY DIAGRAMS

WHEN the number of components in a system is increased to three, the possible total of independent variables is *four*. These are pressure, temperature and two concentration degrees of freedom. In a ternary system, provided the concentrations of two components are known, the third can be implied; thus the composition can be accurately defined with only two concentration variables.

In ceramic systems, vapour pressure, in most cases, can be disregarded and a 'condensed' form of the Phase Rule used to predict the degrees of freedom. When various phases are present in a *three-component* system the maximum variants are as follows:

<i>Phases</i>	<i>Degrees of freedom</i>
1	3 (trivariant)
2	2 (bivariant)
3	1 (univariant)
4	0 (invariant)

The complete graphical representation of a three component phase diagram requires three-dimensional axes and would include all the complexities of the binary systems but translated into three dimensions.

Composition. It is customary to express the composition by means of an equilateral triangle. This is convenient because if A, B and C are the components and the proportions of each are indicated by *a*, *b* and *c* per cent respectively, then,

$$a + b + c = 100 \text{ per cent}$$

in every case. If *a* and *b* are regarded as independent variables, *c* can always be deduced provided the first two are known. The composition of any mixture may conveniently be expressed by three planar axes which intersect at angles of 60° and are parallel to the sides of the triangle.

The apices of the equilateral triangle represent 100 per cent of each pure component; the opposite side of the triangle to any particular apex will be the composition line of mixtures containing zero percentage of the component. Mixtures with intermediate concentrations of any component fall at an appropriate distance between the apex and opposite side. A triangular composition diagram is shown in Fig. X.31. The proportion of the components A, B and C in any particular mixture is easily deduced by drawing lines at convenient intervals across the diagram

¹ Levin, E. M., McMurdie, H. F. and Hall, F. P., 'Phase Diagrams for Ceramists', *Amer. Ceram. Soc. Publ.* (Columbus, Ohio, 1956).

parallel to the three sides. Thus, point P contains 20 per cent of component A, 40 per cent of component B and 40 per cent of component C.

A triangular diagram of this kind offers many advantages, one of which is that if amounts of one compound are progressively added to or subtracted from a ternary mixture whilst the other two components are kept in a fixed ratio, the ensuing change in composition may be represented by a straight line drawn from the appropriate apex through the point of original composition and produced if

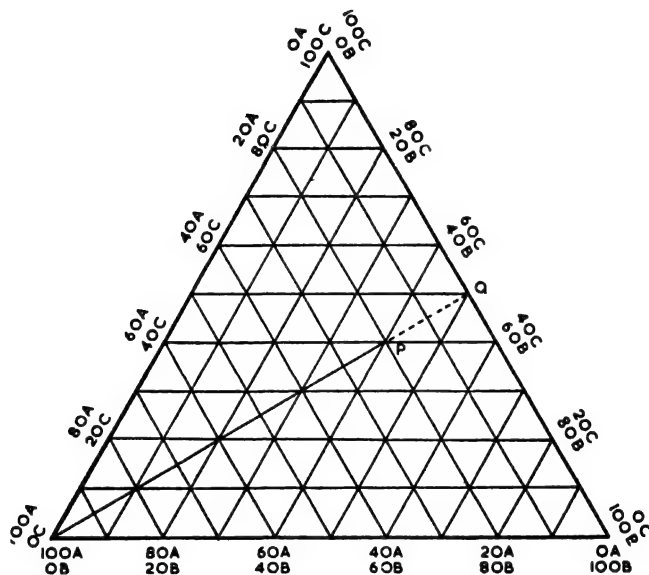


FIG. X.31. THE TRIANGULAR COMPOSITION DIAGRAM OF A TERNARY MIXTURE

necessary. This is shown in Fig. X.31, where the line PA indicates the change in composition brought about by adding amounts of component A to a mixture of composition P (consisting of 20 per cent A; 40 per cent B; 40 per cent C); PQ represents the change in composition of the same mixture when component A is progressively removed. Similar additions or subtractions of the other components of the mixture would result in the composition altering along a line joining the original point P to the corresponding apex of the triangle or to the extension of such a line beyond point P. This is an important fundamental concept which greatly assists in interpreting ternary diagrams.

Another important aspect of the triangular composition diagram is the *gravity-centre principle*¹ for determining the quantitative composition when several phases form from a given mixture. This may be applied to ternary systems in a similar manner to the lever rule in binary mixtures. The point P, for example, is a mixture

¹ That is by using the same geometrical construction as that employed to find the centre of gravity of a plane surface.

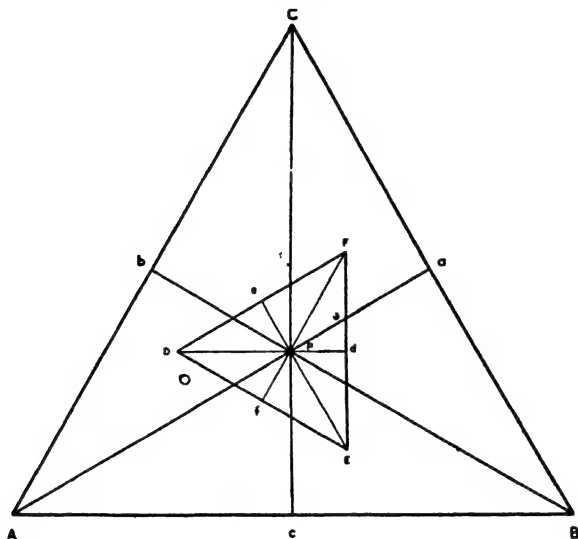


FIG. X.32. ILLUSTRATION OF THE GRAVITY-CENTRE PRINCIPLE FOR CALCULATING THE PHASES IN TERNARY MIXTURES

in the composition triangle A, B, C (see Fig. X.32). If the substances formed during the solidification of the mixture should be the three components A, B, C, the relative amounts of the solid phases are given by the ratios of the intercepts on lines from each apex through P to the opposite side of the triangle, thus

$$A : B : C :: \frac{Pa}{Aa} \quad \frac{Pb}{Bb} \quad \frac{Pc}{Cc}$$

If, however, mixture P separates into three other solid components, say D, E and F, the relative proportions are given by constructing a composition triangle and taking intercepts on the lines from the apices to P produced to the opposite sides of the triangle DEF. Thus

$$D : E : F :: \frac{Pd}{Dd} \quad \frac{Pe}{Ee} \quad \frac{Pf}{Ff}$$

The gravity-centre principle is of value in assessing the relative amounts of phases when compound-formation occurs in ternary mixtures.

Temperature. There remains the problem of representing the third variable in ternary mixtures, namely temperature. This may be solved by introducing an additional axis projecting at right angles from the plane of the triangular diagram. The complete ternary diagram using such a model would be a solid figure bounded by three faces each one based on one side of the composition equilateral triangle and projecting vertically upwards.

Planar diagrams of such solid models can be constructed by representing the temperature as contour lines in a similar way to which height is shown on survey maps.

Phase boundary lines are normally shown by heavy lines, whilst zones of constant temperature or isotherms are in lighter or dotted lines. With a little experience it is not a difficult matter to become familiar with ternary phase diagrams in projection on the equilateral base.

1. Ternary Eutectic Formation. The simplest example of a ternary system is where three components are completely miscible when liquid, but do not mix in any proportion in the solid state. In such a case a *ternary eutectic* is formed which is exactly analogous to that of the binary system on page 545 except that three components are involved.

A perspective drawing of the resulting solid diagram is shown in Fig. X.33A, and the corresponding projection in Fig. X.33B. The addition of any one component to another causes a reduction in the melting point of the latter. In addition, the third component will give rise to a lowering of the melting point of any mixture of the other two components. Hence, the solid diagram is shaped like a well with three troughs falling into the middle (point E_4). Each trough arises at the eutectic point of a binary mixture (points E_1 , E_2 , E_3), and they correspond to phase boundary lines which effectively divide the diagram into three distinct regions. The field bounded by the points A - E_1 - E_4 - E_3 represents the stability range of component A in equilibrium with liquid. When any mixture, the composition of which falls in this field, is cooled the first product of crystallisation will be component A. Similarly component B will be formed first from a mixture in the field B - E_1 - E_4 - E_2 and crystals of C will be the first solid phase to form on cooling a composition in the C - E_2 - E_4 - E_3 field.

In each stability field the isotherms fall towards the eutectic point (E_4) and along the phase boundary lines E_1 - E_4 , E_2 - E_4 , and E_3 - E_4 the temperature also decreases in the direction of the ternary eutectic, E_4 .

A further simplification in representing ternary diagrams consists in dispensing with the isotherms and indicating changing temperatures by arrows on the phase boundary lines, as in Fig. X.33c, which shows the arrows pointing in the direction of decreasing temperature.

The phase boundary lines in the ternary diagram shown in Fig. X.33c, are the positions at which two solid phases can be in equilibrium with liquid. Along the line 1-4, solid A and B can co-exist, B and C may be present together along 2-4 and A and C form simultaneously along the line 3-4. In each of these conditions the system is univariant and has one degree of freedom. At point 4, however, three solid phases A, B and C may be present along with a liquid, hence this is an invariant point and before the temperature can change, one phase must vanish. The ternary eutectic is thus the point of lowest temperature in the system at which a liquid phase can exist.

The crystallisation paths when any mixture is cooled are similar in all parts of a ternary-eutectic system and may be illustrated by a composition N in the stability field of component A (see Fig. X.33c).

The mixture is liquid at all temperatures above the solidus curve. Crystals of A are the first to separate from the cooling melt and in accordance with the principle

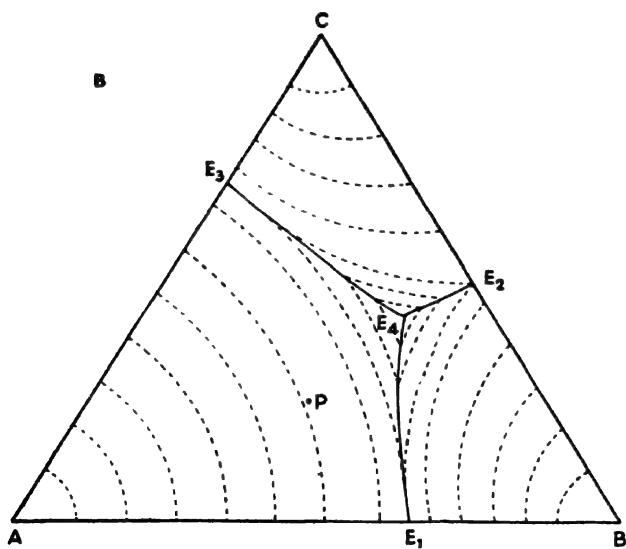
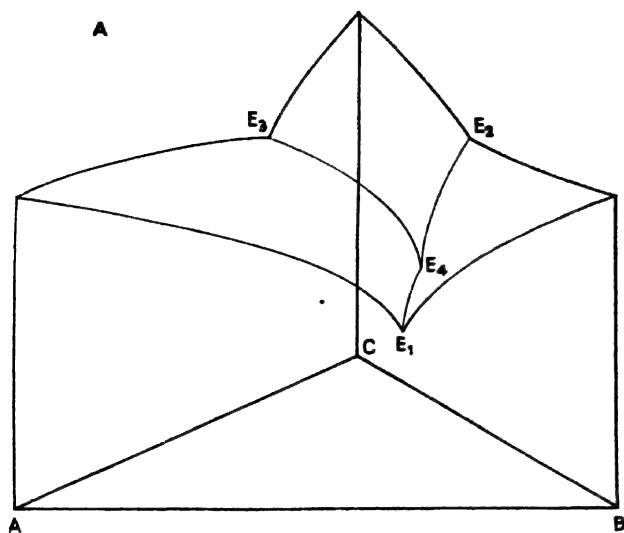


FIG. X.33. THE PHASE DIAGRAMS OF A THREE COMPONENT SYSTEM SHOWING THE FORMATION OF A TERNARY EUTECTIC

A A solid model

B A planar representation showing isotherms

laid down on page 576 the composition of the liquid phase changes along the line NM which is AN produced. When the liquid composition becomes that of the point M on the phase boundary line 1-4, both solid A and solid B can form together and they do so with the liquid composition changing along the line M-4. At the eutectic point 4, crystals of C also separate and eventually all liquid will vanish as the cooling proceeds. The final state is, therefore, a mass of crystals with each solid component a separate entity.

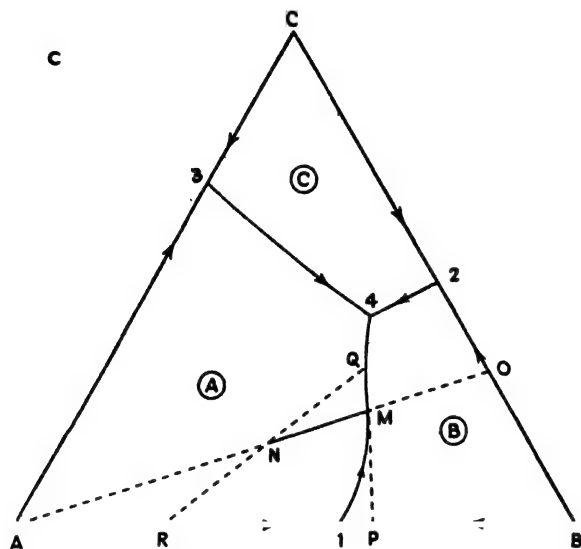


FIG. X.33. THE PHASE DIAGRAMS OF A THREE COMPONENT SYSTEM SHOWING THE FORMATION OF A TERNARY EUTECTIC

c A planar representation with arrows indicating the direction of falling temperature

At any temperature, the relative proportions of each phase present may be calculated by applying the gravity-centre principle. The determination of the amount of component A which crystallises between the initial solidification point N and the phase boundary line at M demonstrates its use.

If ANM is produced it will meet BC at O. The amount of component A in a mixture represented by the point N is given by the ratio ON/OA ; similarly the amount of A in mixture M is OM/OA . The difference in amount of A in the two mixtures would be equivalent to the amount crystallised during the cooling of the initial mixture from the temperature at N to that at M. This may be expressed as:

$$\frac{ON}{OA} - \frac{OM}{OA} = \frac{NM}{OA}$$

The ratio of the amount crystallising to the amount of component A originally present is $NM/OA \div ON/OA = NM/ON$.

Along the phase boundary line 1-4 components A and B crystallise together and the relative amounts being formed at any time are found by taking the tangent to the line at that point, and projecting it on to the AB axis. At M, for example, the tangent cuts AB at P, and by simple extension of the lever principle, the ratio of solid A and B *being formed* is given by:

$$\frac{\text{solid A}}{\text{solid B}} = \frac{\text{PB}}{\text{AP}}$$

The composition of the total solid (components A and B only) *having formed* at any point along 1-4 is given by constructing a line from that point through N the point of original composition, to cut the AB axis. The relative amounts of solid A and B are then given by the ratio of the lengths of the intercepts made on this axis. At point Q, for example, the line of construction is QNR and the composition of the solid phase present at the point Q is given by:

$$\frac{\text{Total A crystallised}}{\text{Total B crystallised}} = \frac{\text{BR}}{\text{AR}}$$

This is so because mixture N has separated into a liquid of composition Q and a combined solid phase. The composition of the solid must lie along QN produced and as it contains only components A and B, it must also fall on the line AB, hence point R is the composition point of the solid. The percentage amount of component A in such a mixture is given by $\text{BR}/100$ and that of B by $\text{AR}/100$. Hence, the ratio of A to B must equal BR/AR .

The *total amount* of components which have crystallised at any point, or conversely the composition of the liquid phase remaining, may be readily calculated from first principles. The percentages of solid A and solid B which have crystallised at point Q from an original mixture N may be deduced as follows:

	A	B	C
Composition of liquid N	<i>a</i> parts	<i>b</i> parts	<i>c</i> parts
At Q the liquid remaining has the composition	<i>d</i> „	<i>e</i> „	<i>f</i> „

As component C does not crystallise up to the point Q, there must be the same amount of this component in the liquid phase at Q as in the original mixture. Hence, *f* must be reduced to the value of *c*, and *d* and *e* must be altered in the same proportion thus:

	A	B	C
Composition of liquid phase at Q	$d \frac{c}{f}$ parts	$e \frac{c}{f}$ parts	<i>c</i> parts

The amounts of A and B which crystallise on cooling to the point Q are:

$$\begin{array}{cc} \text{A} & \text{B} \\ a - d \frac{c}{f} \text{ parts} & b - e \frac{c}{f} \text{ parts} \end{array}$$

or expressed as a percentage of the original amount of component.

$$\begin{array}{cc} \text{A} & \text{B} \\ \left(1 - \frac{dc}{af}\right) 100 & \left(1 - \frac{ec}{bf}\right) 100 \end{array}$$

Alternatively, the relative amounts of phases at the point Q can be determined by the gravity-centre principle. The three phases present have the composition A, B and that of the point Q, hence, a triangle can be constructed with each composition as an apex (Fig. X.32). The relative amounts of the three phases is given by the intercepts on the lines from each apex through P produced on to the opposite side of the triangle. Thus in Fig. X.34:

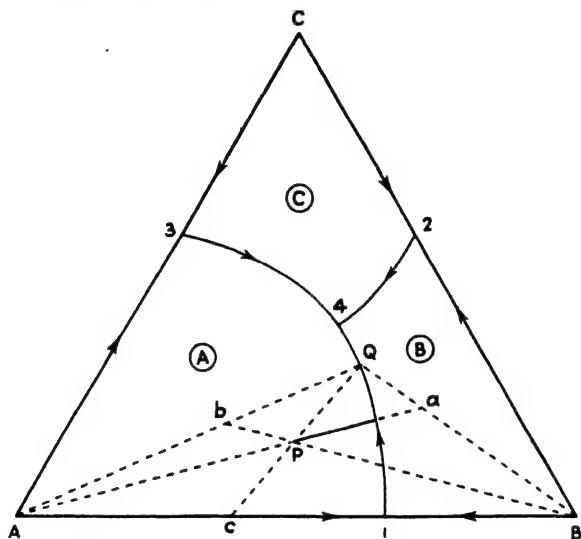


FIG. X.34. THE TERNARY EUTECTIC PHASE DIAGRAM SHOWING THE APPLICATION OF THE GRAVITY-CENTRE PRINCIPLE TO DETERMINE THE COMPOSITION OF PHASES

Ratio of solid A : solid B : liquid of composition Q :: Pa/Aa : Pb/Bb : Pq/Qq

2. Binary Compound Formation without Solid Solution. In many ternary mixtures, two of the components combine together to form a binary compound. There are several variants depending on the nature of the compound:

(a) Where the *binary compound melts congruently* (i.e. without decomposition) over the *whole* field of its existence. The equilibrium diagram is as shown in Fig. X.35. A solid diagram would show a *solidus* (p. 551) declining in temperature from the C apex to the phase boundary line $E_4-E_5-D-E_6-E_3$. This line has as extremities the binary eutectics of mixtures A-C and B-C; there are two points of minimum temperature E_5 and E_6 separated by a 'col' of which D is the maximum point. The centre dome-shaped portion of the E_5-E_6 phase-boundary line is maintained

towards the composition line AB but with temperatures gradually increasing. The phase equilibria conditions along the line AB are of a binary mixture with congruent compound formation as illustrated in Fig. X.7 (p. 550).

A line drawn from the C apex of the composition triangular diagram to the point M which is the composition of the binary compound (A_xB_y) will pass through the point D and effectively divide the diagram into two parts, each of which has the characteristics typical of ternary eutectic formation. The components of the first triangle are A, C, and the compound A_xB_y ; the second triangle has B, C and A_xB_y as components. CDM is known as a *conjugation line* and the temperature varies along its length as in binary eutectic mixtures. The point D is at a minimum temperature with respect to C and M.

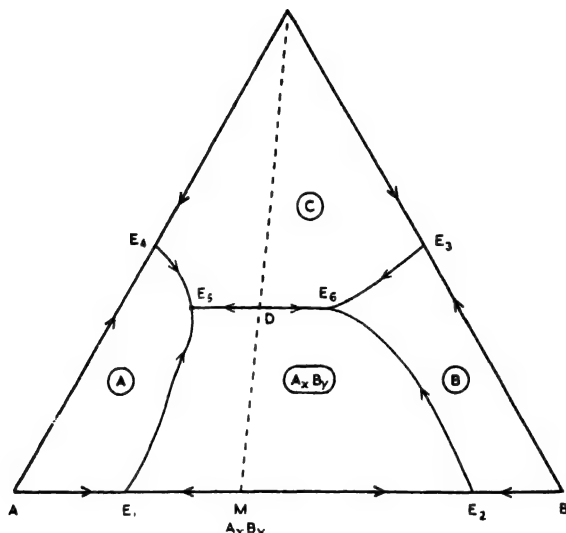


FIG. X.35. THE PHASE DIAGRAM OF A TERNARY MIXTURE WHICH FORMS A CONGRUENT BINARY COMPOUND

The *crystallisation-paths* of any mixture may be interpreted by applying the principles relating to ternary eutectic mixtures. The final products of crystallisation of any mixture are, however, determined by the *conjugation triangle* in which it occurs. Mixtures to the left of the conjugation line CDM can have only A, C and compound A_xB_y as solid products; whilst a mixture in the composition triangle bounded by CMB will crystallise only to solid B, C, and A_xB_y .

(b) Where the *binary compound is stable to its melting point in only a limited field of composition*. As the equilibrium diagram in Fig. X.36 shows, the binary field AB is that of normal, stable-compound formation. The dome-shaped portion does not continue into the ternary field but falls to a *ternary peritectic inflection* P. The phase boundary lines from this point and from the binary eutectic points E_2 and E_3 meet at a ternary eutectic or minimum temperature point E_5 .

A conjugation line from C to the point M (representing the compound A_xB_y),

only of solid B, C and A_xB_y . The relative amounts of each phase in all cases is found by applying the gravity-centre principle (see p. 576), around the point of original composition in the suitable conjugation triangle.

An interesting crystallisation-path is exhibited by a mixture of composition R (see Fig. X.36). The initial crystallisation product will be component A and the liquid will change in composition along Rc until the phase boundary line E_4-P is joined. Solid C then crystallises simultaneously until the liquid reaches the composition of the peritectic P. Four phases can now theoretically exist, for solid A_xB_y begins to form as solid A redissolves in the liquid phase. With this particular mixture, all solid A will vanish and the final products will be solids B, C and A_xB_y . When the composition of the liquid first reaches the point P, however, only solid A and C are present and the ratio of these two phases is given by producing PR to meet the AC axis at d' and by the gravity-centre principle

$$\frac{\text{amount of solid A}}{\text{amount of solid C}} = \frac{d'C}{Ad'}$$

Before the temperature can be lowered from that of the peritectic point, all solid A must redissolve whilst compound A_xB_y crystallises. Finally, only solid A_xB_y and solid C can remain and the relative amounts of these are found by taking the ratio of the intercepts on the conjugation line CM of PR produced to d'' . thus

$$\frac{\text{amount of } A_xB_y}{\text{amount of C}} = \frac{d''C}{Md''}$$

It is important to note that, during this process, the liquid phase remains at constant composition (P) but is gradually reduced in amount.

The converse process of heating a solidified mixture of composition R well illustrates the meaning of the ternary peritectic point. Solids B, C and A_xB_y which are the solid phases of mixture R begin to melt at the temperature of E_5 . At the temperature of point P, the compound A_xB_y dissociates into solid A and liquid and thus decomposes at temperatures below its true melting point M.

(c) Where the *binary compound is unstable to its melting point over all ranges of composition*. In other words there is both *binary and ternary peritectic formation*; the equilibrium diagram is shown in Fig. X.37.

The conjugation line CM lies outside the field of stability of the compound A_xB_y at all points and the binary system AB which contains a peritectic point P_1 is identical with the system illustrated in Fig. X.6 (p. 548). The point P_2 is a ternary peritectic point similar in all respects to the point P in the previous section (Fig. X.36).

Once again the position of a mixture relative to the conjugation line CM determines the final products of crystallisation although the processes involved during equilibrium cooling of certain mixtures are rather more complex.

The crystallisation path of a mixture of composition a' to the left of the conjugation line CM, illustrates many of the principal features.

As ' a ' lies in the stability field of component A, this will be the first product of crystallisation and the liquid composition will proceed along the line Aa' produced

until the phase boundary line P_1P_2 is reached at b . The compound A_xB_y will then form also, but the solid A already crystallised will begin to redissolve. This is so because the tangent to the phase boundary line P_1P_2 at b cuts the AB axis at D which is outside the A/ A_xB_y stability line. The re-resolution of A continues until the liquid composition reaches P_2 which is an invariant point. As the mixture ' a ' lies within the A-C- A_xB_y conjugation triangle, some solid A must remain after all the liquid phase has crystallised into solid C and compound A_xB_y .

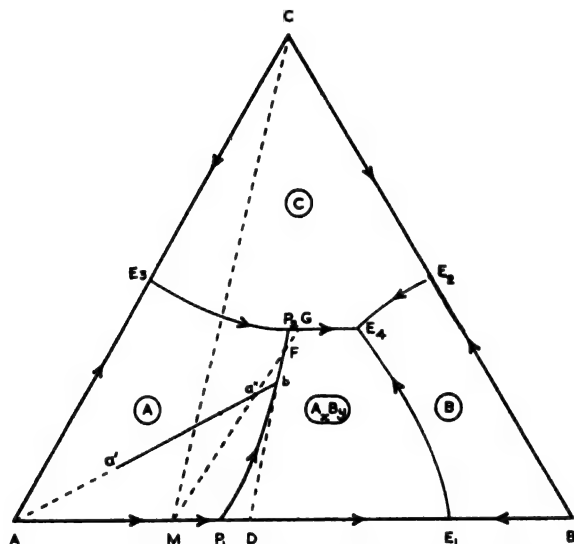


FIG. X.37. THE TERNARY DIAGRAM SHOWING THE FORMATION OF A BINARY COMPOUND WHICH IS INCONGRUENT AT ALL COMPOSITIONS

If the original mixture had the composition of the point a'' , however, although solid A would still be the original phase to form, it would completely redissolve whilst the liquid composition was progressing along bP_2 . The position at which all solid A disappears may be predicted by producing a line from M (the composition of the compound A_xB_y), through a'' to F on the phase boundary line P_1P_2 . Fa'' produced thus intersects the A- A_xB_y composition line at a point corresponding to 100 per cent of the A_xB_y phase which must be the composition of the solid which has crystallised when the liquid corresponds to the point F. Further cooling of a mixture of original composition a'' will result in crystallisation of more A_xB_y and no other solid form. Hence, the liquid phase will follow the composition of the line MF produced across the phase field A_xB_y . When this line cuts the phase boundary line P_2E_4 , solid C will also crystallise and the liquid composition will move to E_4 , a ternary eutectic. At this temperature, all liquid will vanish to form solid B, C and compound A_xB_y .

Examples are known where the phase boundary line P_1P_2 is so shaped that recurrent crystallisation of the initial solid phase takes place. Fig. X.38 illustrates a

system which would exhibit this phenomenon. The crystallisation path of a mixture a' would be along $a'o$ with solid A separating. The liquid composition would then follow the phase boundary line P_1P_2 to the point b with A_xB_y only being crystallised and solid A redissolving. At b no crystals of A remain and the crystallisation path follows along $Ma'b$ produced, with only solid A_xB_y being formed. This line, however, again cuts the phase boundary line P_1P_2 at c . Solid A can now be reformed because the tangent to P_1P_2 at c cuts the AB axis between A and A_xB_y , indicating that both solid forms can co-exist. It is only when the liquid composition reaches the peritectic point P_2 that solid A becomes unstable again and redissolves in the liquid.

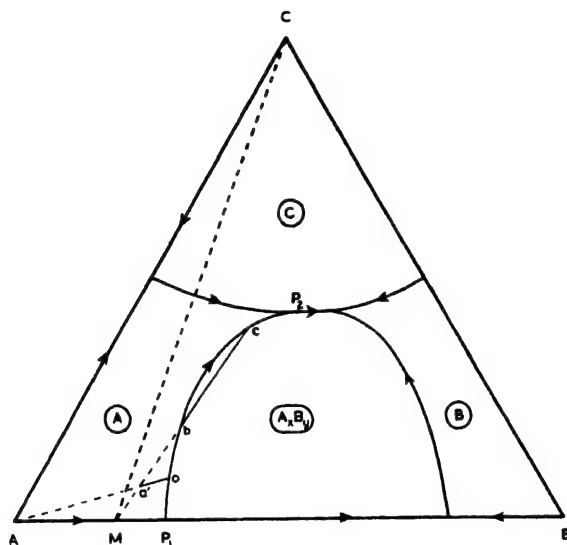


FIG. X.38. A TERNARY PHASE DIAGRAM SHOWING RECURRENT CRYSTALLISATION OF ONE PHASE

(d) Where a *binary compound* is stable only when it is formed above a certain *minimum temperature*, as shown in Fig. X.39.

The compound A_xB_y melts congruently in the binary field AB at M, but in the ternary field *below* the temperature of the point D it is not a stable phase.

(e) The converse case where a *binary compound dissociates* above a certain *temperature* is also known and the consequent equilibrium diagram is shown in Fig. X.40.

In the binary field AB the compound A_xB_y does not form but if a ternary mixture is cooled which intersects a phase boundary line of the compound A_xB_y below the temperature of the point D, the binary compound will crystallise. On heating any mixture containing the compound A_xB_y complete dissociation will take place at the temperature of D.

An example of this phenomenon is found in the ternary system



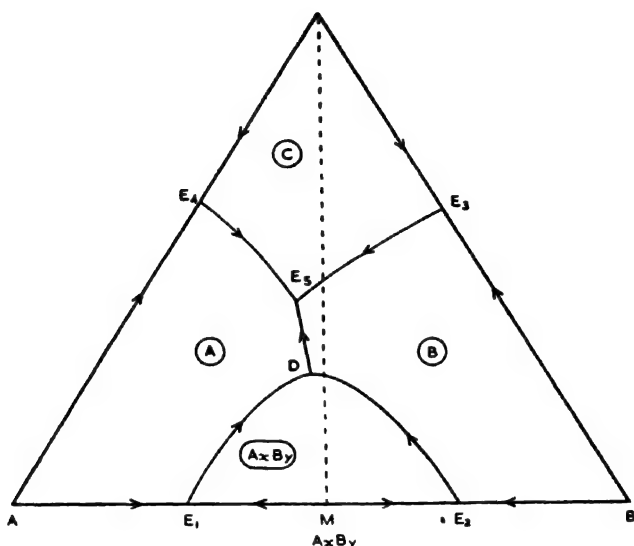


FIG. X.39. A TERNARY PHASE DIAGRAM SHOWING THE FORMATION OF A BINARY COMPOUND WHICH IS STABLE ONLY ABOVE A CERTAIN MINIMUM TEMPERATURE

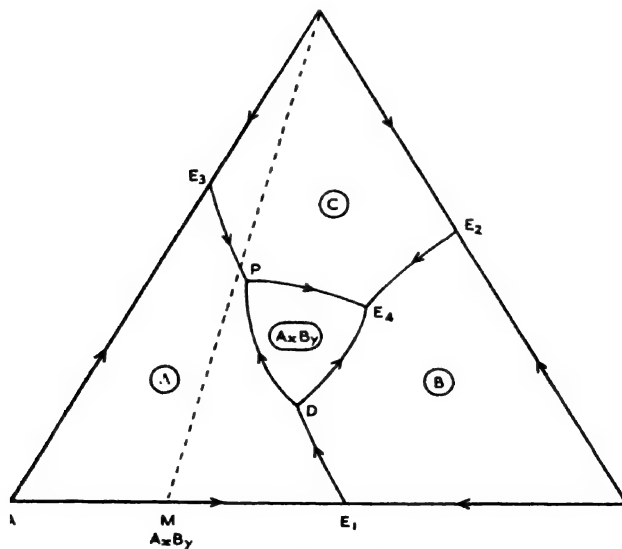


FIG. X.40. A TERNARY PHASE DIAGRAM SHOWING THE FORMATION OF A BINARY COMPOUND WHICH DISSOCIATES ABOVE A CERTAIN TEMPERATURE

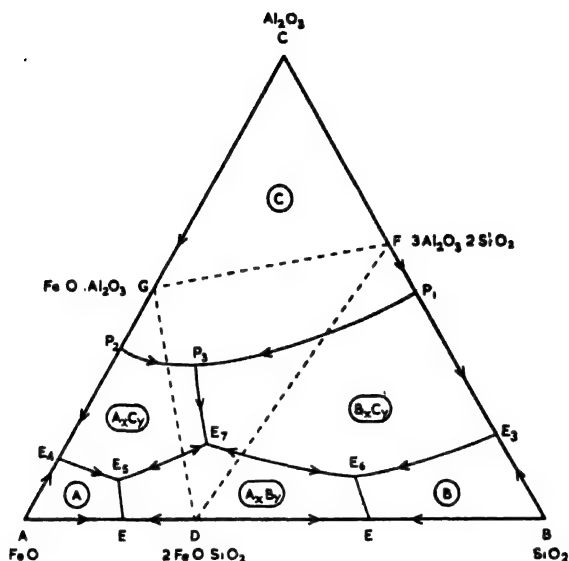


FIG. X.41. A SIMPLIFIED FORM OF THE PHASE DIAGRAM OF THE COMPONENTS $\text{FeO}/\text{Al}_2\text{O}_3/\text{SiO}_2$ SHOWING COMPOUND FORMATION

Tricalcium silicate, $3\text{CaO} \cdot \text{SiO}_2$, does not form in the binary field $\text{CaO}-\text{SiO}_2$ but does separate over a narrow range of composition if Al_2O_3 is also present (see Fig. X.50).

(f) *Multiple binary compounds* may form in a ternary mixture but each form can be separated into one or other of the five previously discussed types.

A ternary mixture containing two incongruent and one congruent binary compounds is the $\text{FeO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system. Both $\text{FeO} \cdot \text{Al}_2\text{O}_3$ and $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ decompose before melting but $2\text{FeO} \cdot \text{SiO}_2$ is stable to its melting point. A simplified form of the equilibrium diagram in this region is shown in Fig. X.41.

The conjugation triangles enable the final, solid phases after equilibrium cooling to be predicted. For example, a mixture, the composition of which lies in the triangle bounded by DGF, will produce only the three compounds in ratios which may be determined by the gravity-centre principle.

3. Ternary Compound Formation without Solid Solution. When three components are present in a mixture, ternary compounds of the general composition $\text{A}_x\text{B}_y\text{C}_z$ may be formed. There are two general cases to be considered depending on whether the compound is stable to its melting point (i.e. congruent) or whether it dissociates prior to melting (incongruent).

(a) *Congruently melting compound formation* is characterised by an equilibrium diagram which in the solid form would have a dome-shaped centre. From the maximum temperature point the isotherms would fall away to three ternary eutectic

points. The solid form and projection models with and without isotherms are shown in Fig. X.42A, B, C.

The insertion of the conjugation lines AM, BM and CM divides the diagram into three simple areas of ternary eutectic formation. The three components of each conjugation triangle are, in each case, two of the primary components plus the ternary compound. There are three binary eutectics E_1 , E_2 and E_3 and three ternary eutectics at E_4 , E_5 and E_6 .

The final, solid phases crystallising from any ternary mixture are determined from the appropriate conjugation triangle and the relative amounts present by applying the gravity-centre principle within that triangle.

The crystallisation path of any mixture is similar to that in a ternary eutectic system. Mixture R, for example, in the stability field of component A (Fig. X.42c) will, at the solidus temperature, form solid A. The liquid composition will follow the line AR produced to S on the phase boundary line E_4E_6 ; the compound $A_xB_yC_z$ will then also form and the liquid will proceed in composition along E_6E_4 to the ternary eutectic invariant point where the liquid phase will vanish to leave solid A, B and compound $A_xB_yC_z$.

(b) When the *ternary compound melts incongruently* the composition point of the compound falls outside its field of stability as shown in Fig. X.43.

A line from A through M (the composition of the compound) will meet the phase boundary line FE_4 at D. This point will be at a maximum temperature and the isotherms will fall away to the ternary eutectic E_4 and 'transformation point F'. A similar maximum occurs on the phase boundary E_4E_6 at the intersection of CM, but as BM does not cut FE_6 there is no maximum temperature point along this phase boundary.

The crystallisation-paths in a ternary system with an incongruent, triple compound resemble those in the ternary system with a binary compound which dissociates below its melting point over all the composition range (see Fig. X.39, p. 588). A mixture of composition a' within the conjugation triangle AMB forms solid A as the initial phase and the liquid composition proceeds to b which lies between D and F on the phase boundary curve E_4F . The tangent to this curve at b indicates that solid A is an unstable phase, hence crystallisation proceeds with the formation of compound $A_xB_yC_z$ and re-resolution of solid A. At F, solid B can also form which would be a fourth phase; hence F is an invariant point. Because a' , the composition of the original mixture, lies in the conjugation triangle AMB, all liquid must vanish at the temperature of F because only solid A, B and $A_xB_yC_z$ can be present in the final crystallised mixture.

Should a composition a'' within the conjugation triangle CMB be crystallised, all solid A formed in the original stages would redissolve when the liquid had the composition of the point C_1 . Solid $A_xB_yC_z$ is the only stable solid phase, hence the crystallisation path leaves the phase boundary line and proceeds across the stability field of the compound until the phase boundary line FE_6 is reached at d . Solid B is then simultaneously crystallised until the ternary eutectic point E_6 , where solid C also forms and the liquid phase vanishes.

Many examples of congruent and incongruent compound formation will be given in the systems shown in Figs. X.50–53 and although many mixtures appear

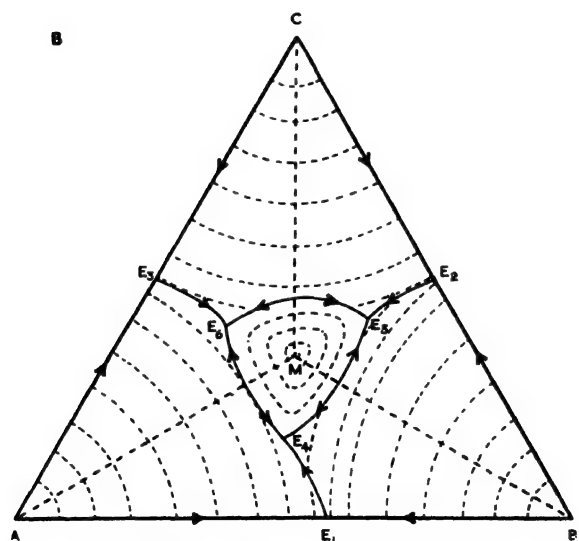
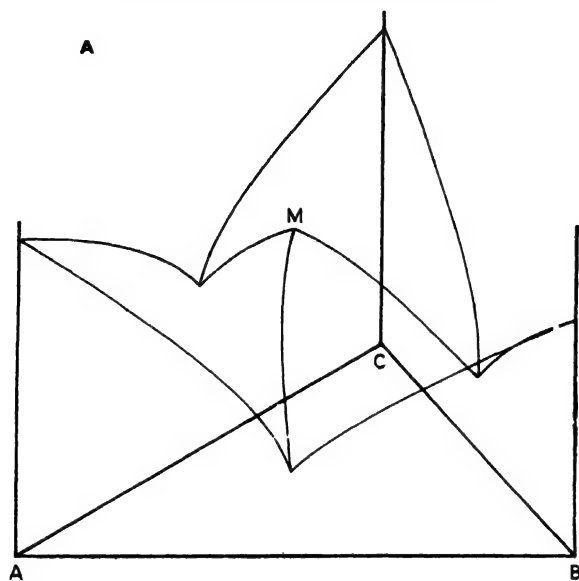


FIG. X.42. THE PHASE DIAGRAM OF A THREE-COMPONENT MIXTURE SHOWING THE FORMATION OF A TERNARY COMPOUND

A A solid model

B A planar representation with isotherms

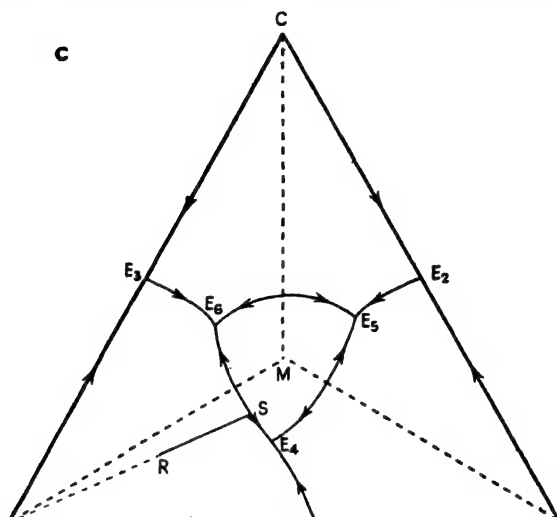


FIG. X.42. THE PHASE DIAGRAM OF A THREE-COMPONENT MIXTURE SHOWING THE FORMATION OF A TERNARY COMPOUND
c A planar representation with arrows indicating the direction of falling temperature

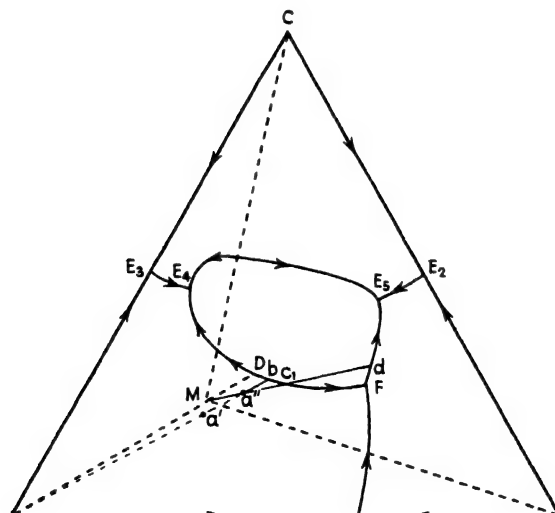


FIG. X.43. A TERNARY PHASE DIAGRAM WITH A TERNARY COMPOUND WHICH MELTS INCONGRUENTLY

complex, if each part is considered separately, it may be resolved into one of the types described in the previous sections.

It is not always convenient to decide which fundamental oxides form the components of many ternary systems because many compounds may form which would give rise to a complicated diagram. In many cases a simplification in representation may be possible by selecting a *congruent* compound as a component and thereby studying only a partial system.

The *crystallisation phenomena of a complex ternary diagram* can be deduced by applying the general principles which have already been described. These may now be summarised as:

1. The first solid phase to appear from a melt is the primary phase for the part of the system in which the melt composition lies.

2. The liquid phase changes along the extension of a line joining the composition point of the primary crystallising phase to that of the composition of the original melt.

3. Only one phase will crystallise until the liquid composition line meets a phase boundary line.

4. At a phase boundary line which divides the stability field of two constituents, the second primary phase will crystallise, and the liquid composition will proceed along the phase boundary line.

5. The ratios of the two primary phases which crystallise at any one instant at a certain temperature along a phase boundary line may be predicted by taking the tangent at that point and measuring the ratio of its intercepts on the line joining the compositions of the primary phases. Should the tangent not cut this line, one of the phases is unstable and will be redissolving.

6. The relative amount of each solid phase which has formed at any point on the crystallisation path may be predicted by joining that point to the original composition of the melt and producing to the line linking the compositions of the phases which have crystallised.

7. If, whilst the liquid composition is following a phase boundary, an unstable primary phase is completely redissolved, the liquidus will leave the phase boundary line and proceed across the stability field of the crystallising phase until another phase boundary line is encountered.

8. The final products of crystallisation are governed by the conjugation triangle (p. 583) in which the composition of the original mixture lies.

9. The crystallisation path always ends at an invariant point within the conjugation triangle when three solid phases are in equilibrium with a liquid.

10. The relative proportions of the final phases on crystallisation are found by applying the gravity-centre principle.

Ternary Systems with Solid Solutions. Ternary systems in which solid or crystalline solutions are possible between all three components present many complex problems. Many examples of this type of phenomena are known in silicate systems; compound formation frequently occurs simultaneously and adds further complications.

The quantitative assessment of solid solution in ternary silicate systems is so difficult that relatively few mixtures have been fully investigated. Most of the

present day information has been implied from research into metallurgical systems and in his classical treatise F. A. H. Schreinermakers has discussed the most important types of crystalline-solution ternary diagrams. Although it is more than likely that complex solid solutions form in many ternary silicate and other ceramic systems, most investigators have not been able to consider this possibility and in most cases all deductions have been made on the basis of a completely immiscible solid state.

It is not within the scope of this volume to describe all the phenomena associated with ternary systems containing solid solutions, but a few of the main features may be mentioned briefly:

1. *Three components completely miscible in both liquid and solid states and no complex formation.*

This simple case is where the binary system illustrated in Fig. X.8 (p. 551), is projected into three dimensions. The perspective diagram is illustrated in Fig. X.44A and, as would be expected, there is a solidus- and liquidus-boundary throughout the whole range of ternary composition. Thus, there is a particular solid composition in equilibrium with each liquid mixture at each solidification temperature.

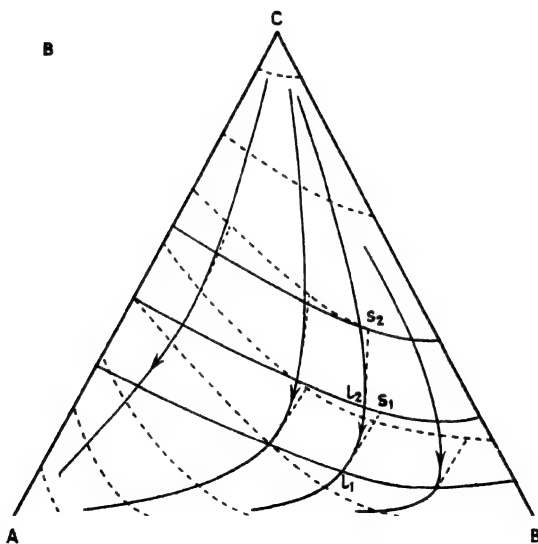
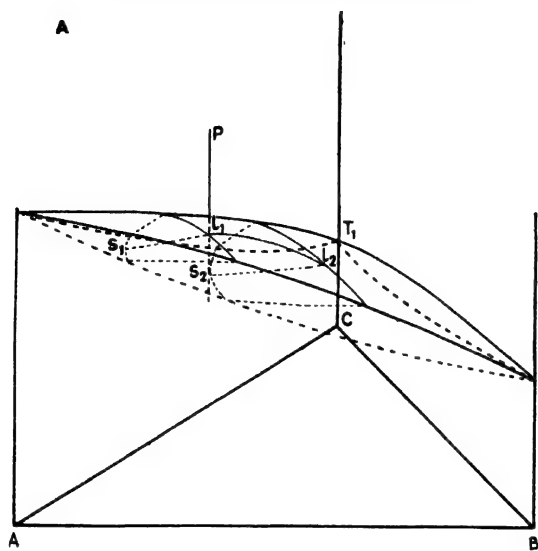
Above the liquidus field, only one phase is present, namely a completely homogeneous melt; whilst below the solidus field the only phase is a homogeneous solid solution. Only between these two fields can two phases co-exist at one temperature. For any particular temperature between the fusion points of the highest and lowest melting components, an isotherm can be drawn which encircles the liquidus and solidus areas. Such a section indicates the composition relationships between two co-existing solid and liquid phases. A line drawn through an isothermal section from a certain liquid composition to the solid in equilibrium with it is called a *conode* or *tie-line*.

The principal features of the system may be more clearly demonstrated by considering the cooling phenomena associated with a specific melt.

A mixture of composition P will be a homogeneous liquid at temperatures above T_1 on the liquidus field. At this temperature, a solid phase will begin to separate with a composition S_1 indicated by the tie line l_1-S_1 . The liquid phase will then change in composition and follow a path on the liquidus area to l_2 . As the temperature is lowered the solid phase in equilibrium with the liquid will also change in composition and ideally, if equilibrium conditions are maintained, the solid phase will be continually redissolving and precipitated again with a slightly different composition. The relative amounts of solid and liquid phases at any temperature are found by applying the *lever principle* (see p. 546) around the vertical line through P to the equivalent solidus and liquidus points. When the solid being formed has assumed the composition of the initial melt, the liquid phase will completely disappear, leaving only a solid phase.

If, as is most usual in silicate systems, cooling does not proceed under equilibrium conditions, the solid phase will not completely readjust its composition as the temperature decreases. As a result, successive layers of solid, each with a different composition, are formed and give rise to *zoned crystals*.

It is difficult to represent completely a ternary system with solid solution in a planar diagram when the temperatures are shown as 'contour lines'. Not only is it essential to have some means of indicating liquidus temperatures for all compositions,



but tie-lines giving the liquidus and solidus equilibrium conditions must be included at numerous points. It is also advantageous to know the crystallisation paths, or the change in composition of the liquid phase, at many positions on the diagram. At the same time, the planar diagram must indicate any phase boundary lines which arise as a result of complex formation.

A projected model of the system of three components with complete miscibility in the solid state is shown in Fig. X.44b. The isotherms are shown as dotted lines and indicate that the pure component C has the highest melting point with B intermediate and A with the lowest fusion point. Crystallisation paths are shown in heavy type and denote the change in composition of specific melts when they crystallise. Two sets of tie-lines are also shown, liquid phase l_1 for example will be in equilibrium with solid S_1 ; liquid l_2 with solid S_2 . For a complete interpretation of cooling phenomena, information of this type would be required for the entire diagram.

In silicate systems, ternary mixtures with complete solid miscibility of simple type are rare, although examples are known where a maximum or minimum point occur. The precise physical meaning of such phenomena has not yet been established with certainty, but inflection points might represent a change-over in solid solution type (see p. 549). At a maximum or minimum, the solid and liquid phases in equilibrium have the same composition and should a melt of that particular composition be cooled, solidification will be complete at one temperature.

The best-known example of this kind of behaviour occurs in *melilites* which are frequently found in basic slags. These are part of the quaternary system CaO , MgO , Al_2O_3 , SiO_2 but the three congruent compounds $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ (*gehlenite*), $2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$ (*akermanite*) and $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ (*sarcolite*), may be regarded as the components of a ternary system. In the separate binary fields, maxima occur between gehlenite and sarcolite, and akermanite and sarcolite, but a minimum point is present in the gehlenite and akermanite series. A combination of these effects translated into the ternary system results in 'saddle-formation' as in Fig. X.45a; the projected drawing showing isotherms and crystallisation paths is in Fig. X.45b.

2. Binary Solid Solution in Ternary Systems. It is not an unusual occurrence for only two components of a ternary system to admix in the solid state whilst the third component separates on cooling, as an independent phase. The simplest case is where components A and B form a homogeneous solid phase over the whole composition range, but both exhibit immiscible binary eutectic formation with the third component C.

A spacial equilibrium diagram for such a system is shown in Fig. X.46a, with the projection giving crystallisation paths and the phase boundary line in Fig. X.46b.

Within the composition field bounded by CE_1E_2 the stable solid phase is component C and when this crystallises, the liquid composition changes linearly (see p. 576). The area bounded by ABE_1E_2 is the field in which binary solid solutions of A and B separate from a melt and hence the crystallisation paths are curved. Because component A has a higher melting point than B, the initial crystallisation products will be richer in this component and the liquid phase will be progressively enriched in component B. The line E_1E_2 is a phase boundary curve along which two phases, solid C and solid solution A-B are in equilibrium. E_1 is at a lower temperature than

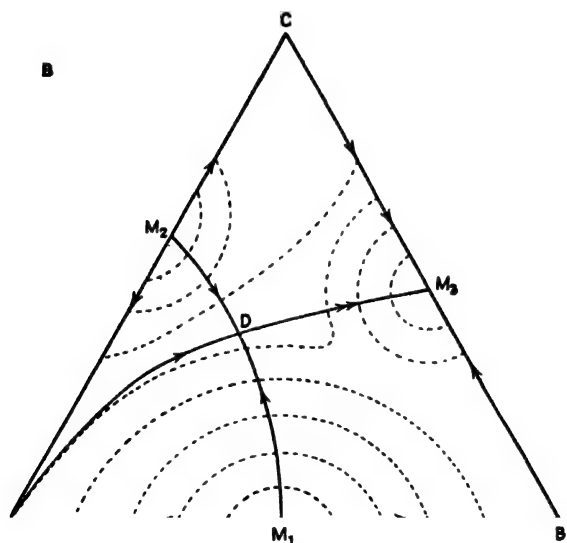
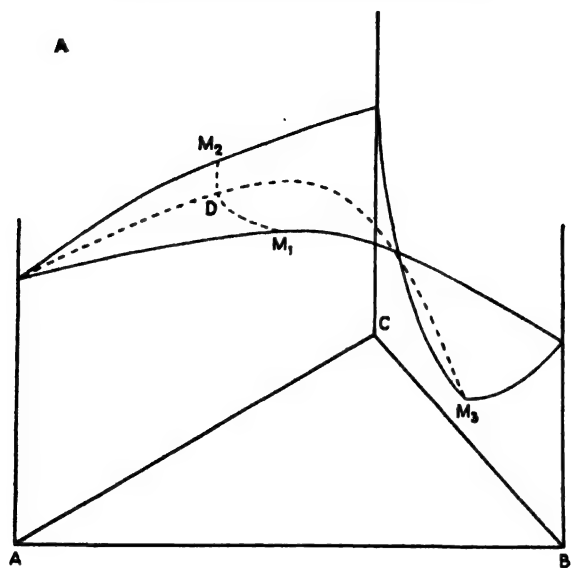


FIG. X.45. A TERNARY PHASE DIAGRAM WHERE THE THREE COMPONENTS ARE COMPLETELY MISCIBLE IN BOTH THE LIQUID AND SOLID STATES, BUT WITH A MINIMUM POINT

A The solid model showing only the liquidus lines

B A planar representation

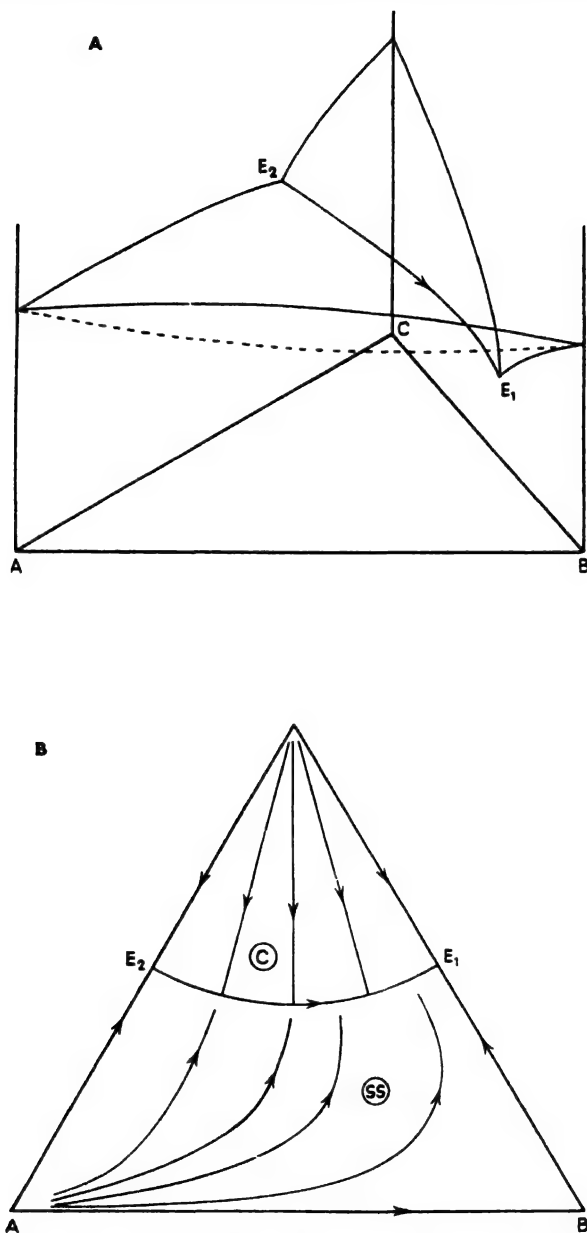


FIG. X.46. THE PHASE DIAGRAM OF A TERNARY MIXTURE WHERE TWO COMPONENTS FORM SOLID SOLUTIONS

A A solid model

B A planar representation

E_2 . The tie-lines, indicating the composition of solid phase in equilibrium with a liquid melt in the field of binary solid solution, will terminate at a point on the solidus line between A and B.

The crystallisation phenomena which occur on cooling a melt P is illustrated by Fig. X.47. When the temperature is lowered to that of the liquidus the crystallising

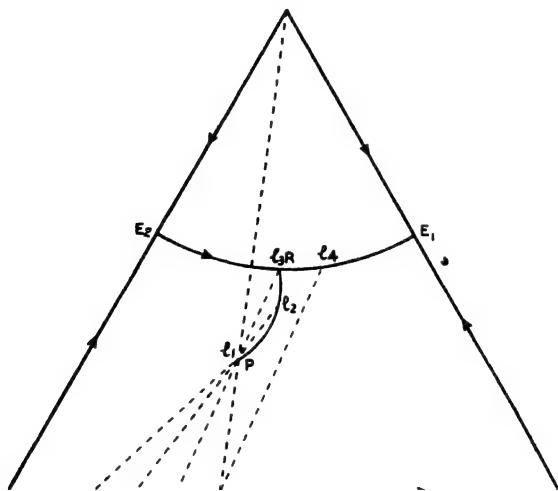


FIG. X.47. ILLUSTRATING THE CRYSTALLISATION STAGES OF MIXTURES IN FIG. X.46

phase is a solid solution of A-B, the composition of which is given by S_1 which is the intersection of the tie-line l_1S_1 on AB. The liquid composition changes along the crystallisation path PR and if the cooling is carried out under equilibrium conditions the solid phase will also change. At the point l_2 , for example, the composition of the homogeneous solid solution in equilibrium is given by producing the line joining l_2 and P to meet the AB axis; S_2 represents the composition of the solid phase in equilibrium with liquid l_2 . When the liquid composition (l_3) reaches the point R on the phase boundary line E_1E_2 , the solid phase is shown by the point S_3 . Now solid component C also separates and the final solidified state will be composed of this component and a solid solution of A-B. The lever-principle (p. 546) applied around the point of original composition P shows that the solid solution S_4 and component C will be the final states and if the tie-lines of the system are known, the composition of the final liquid, prior to complete crystallisation may be predicted as l_4 .

The ternary system *diopside*, *albite* and *anorthite* provides a typical example of binary solid solution in a three component mixture. The two plagioclase feldspars are considered by Bowen to be completely miscible in the solid state over the whole range of composition, but form binary eutectics with diopside.

Binary Compound Formation with Solid Solution. An important extension of ternary solid solution diagrams is where a binary compound A_xB_y is formed which

is miscible in the solid state with component C. The type of diagram depends upon the nature of the compound, which may be congruent (melts stably) or incongruent (decomposes prior to melting).

When a congruent compound forms a solid solution with the other component, the phase diagram is relatively simple and is as illustrated in Fig. X.48. The solid solution phase is composed of varying amounts of component C and compound A_xB_y , so the composition will have the general form: $aC.bA_xB_y$, where $a + b = 1$. The ratio of components A and B in solid solution is thus always the same and equal to $x:y$.

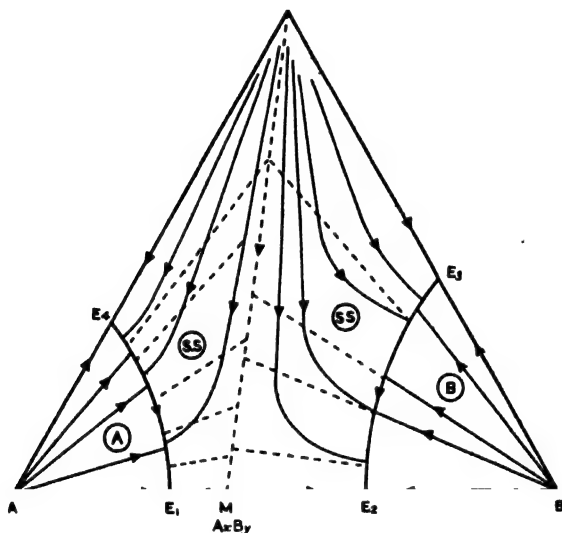


FIG. X.48. THE PHASE DIAGRAM OF A TERNARY MIXTURE WHERE A BINARY COMPOUND IS PRODUCED WHICH FORMS SOLID SOLUTIONS WITH THE THIRD COMPONENT

The conjugation-line CM effectively divides the diagram into two systems each of which is that of a binary solid solution in a ternary mixture (Fig. X.46).

Mixtures to the left of CM in the conjugation-triangle ACM will crystallise to solid A and a solid solution of $C-A_xB_y$, whilst mixtures in the triangle BCM form solid B and a solid solution of $C-A_xB_y$.

When the binary compound (A_xB_y) is *incongruent* the equilibrium diagram of the ternary system is as shown in Fig. X.49A, in which the binary field AB has a peritectic point P and there are two phase-boundary curves where solid solution $C-A_xB_y$ crystallises simultaneously with either the A or B component. The conjugation line CM, however, is not entirely within the stability field of the solid solution and over the range MD, the $C-A_xB_y$ complex would dissociate before melting by virtue of the decomposition of the compound A_xB_y .

The crystallisation of certain mixtures making use of the crystallisation paths and tie-lines of Fig. X.49A, is shown in Fig. X.49B. A mixture of composition 'a'

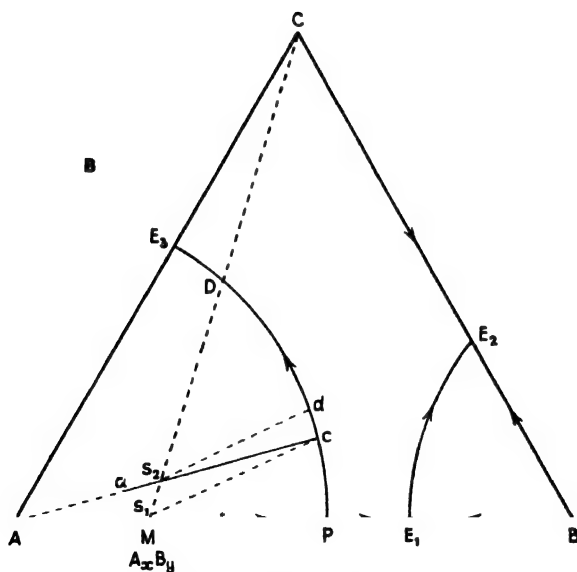
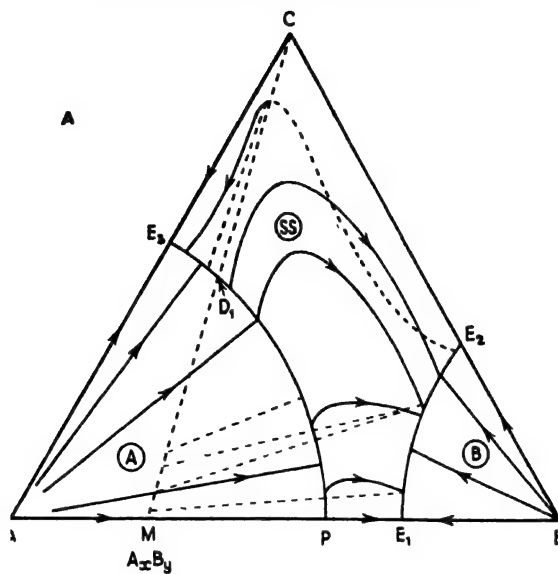


FIG. X.49. THE PHASE DIAGRAM OF A TERNARY MIXTURE WHERE A BINARY COMPOUND WHICH FORMS SOLID SOLUTIONS WITH THE THIRD COMPONENT, MELTS INCONGRUENTLY

(within the conjugation triangle AMC) will initially form solid component A. The liquid composition will follow Az produced until the phase boundary curve PE_3 is joined at c where a solid solution of composition S_1 also separates. At this point, solid A is an unstable phase (p. 593) hence it is continually being redissolved as the liquid changes in composition along PE_3 . The solid solution being formed also changes composition until at some point d on the phase boundary curve, solid solution S_2 is the equilibrium composition. At this point, all remaining liquid must vanish because if, as predicted by the conjugation triangle ACM , a melt of composition 'a' is to separate into component A and a solid solution along CM , these two phases will be A and S_2 (see gravity-centre principle, p. 576).

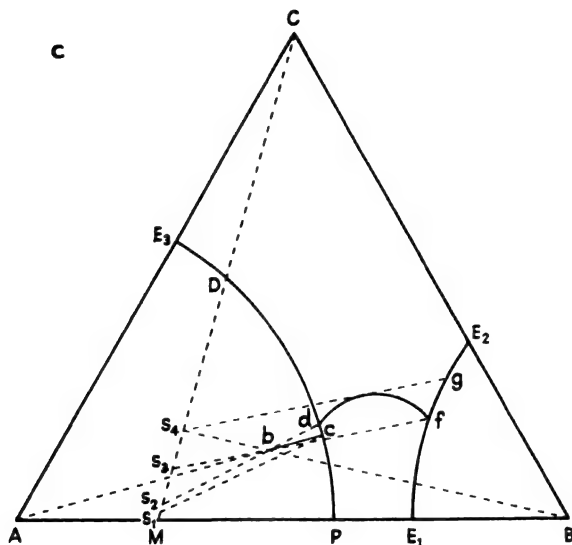


FIG. X.49. THE PHASE DIAGRAM OF A TERNARY MIXTURE WHERE A BINARY COMPOUND WHICH FORMS SOLID SOLUTIONS WITH THE THIRD COMPONENT, MELTS INCONGRUENTLY

A mixture of composition b (within the conjugation triangle CMB) again crystallises component A initially to the point c (Fig. X.49c). The liquid composition, as before, changes along PE_3 with resolution of A and precipitation of a solid solution until at some stage d all solid A will have disappeared. Because only one solid phase is now stable, the liquid composition leaves the phase boundary curve PE_3 and progresses across the field, still precipitating a solid solution which is continually changing its ratio of $C:A_xB_y$. At some temperature, the composition of the liquid joins the phase boundary E_1E_2 at f , where the equilibrium solid solution has the composition of the point S_3 . At f , solid B also separates and the liquid changes along fE_2 until at some point it disappears completely. This will be given by g where the equilibrium solution has the composition S_4 . The final solid contains only component B and a solid solution $C-A_xB_y$, hence the extremes of a line from B

through *b* (the point of original composition) to CM will represent the final solid phases.

The relative amounts of these two phases are given by the relationship:

$$\frac{\text{solid B}}{\text{solid solution (composition } S_4\text{)}} = \frac{bS_4}{Bb}$$

Ternary systems with solid solution phenomena are known where complex formation is even more involved than the examples already quoted. It is beyond the scope of this volume to include such systems although it may be emphasised that many silicate systems fall into the category. The reader who wishes to pursue this subject further is referred to the works of Schreinemakers, Bakhuis and Roozeboom, Vogel, Eitel and others.

TERNARY SYSTEMS IN CERAMIC MATERIALS

It is impossible to include in this volume all the ternary systems which are of importance in ceramic materials. For more detailed information the reader should consult *Phase Diagrams for Ceramists*, published by the American Ceramic Society (see p. 575).

Some examples are:

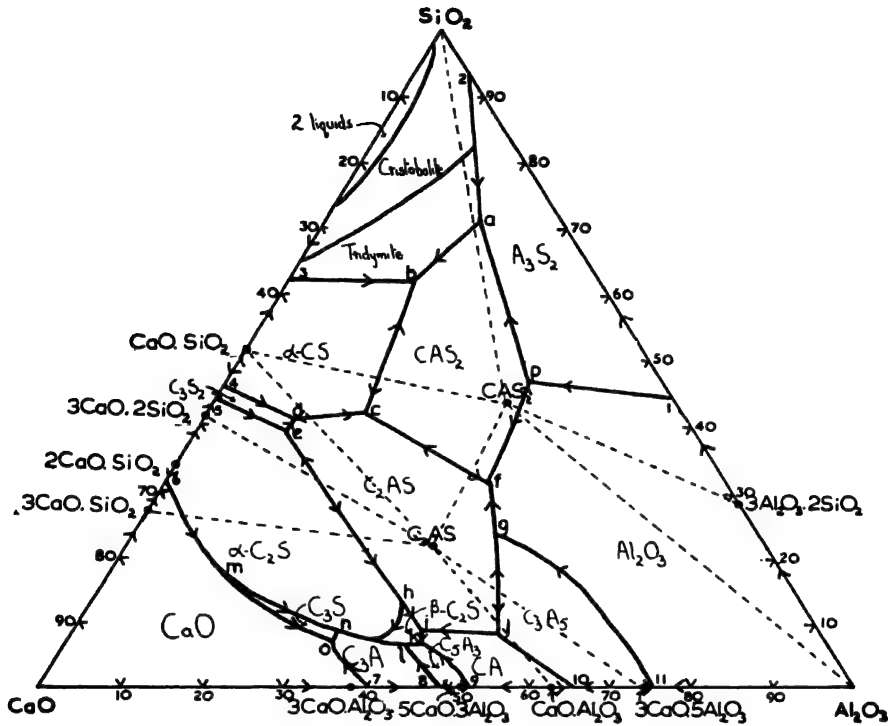
The **lime-alumina-silica** equilibrium diagram (Fig. X.50) has been deduced by Rankin and Wright¹ and although it appears highly complex, the phases which would crystallise from any mixture of components can be deduced by drawing the conjugation triangle embracing three adjacent phases and applying the principles laid down in the preceding pages.

There are nine binary and two ternary compounds formed in the system as follows:

Binary Compounds

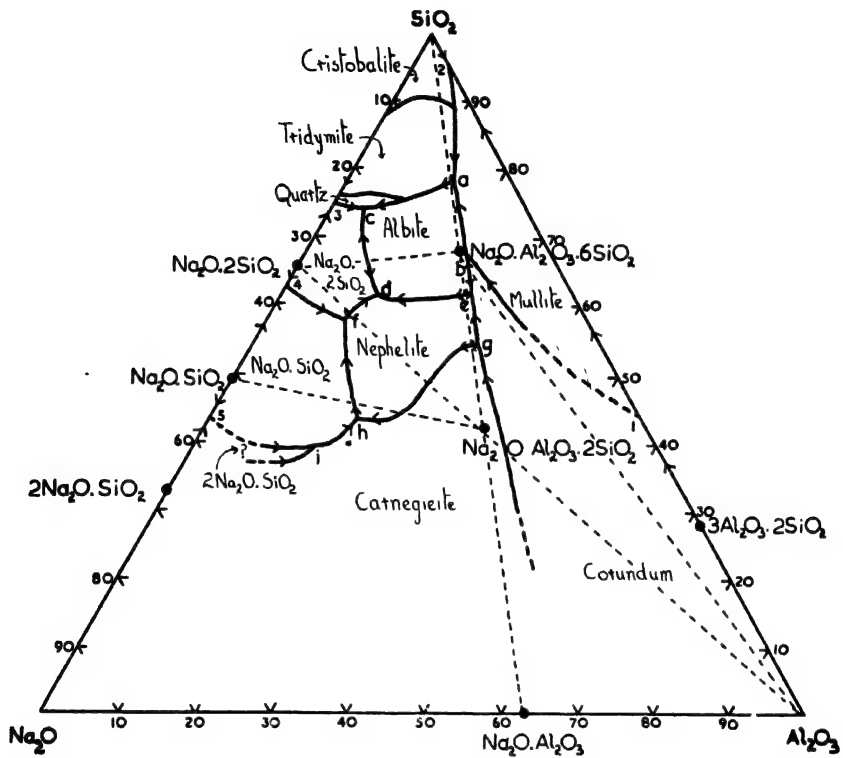
3CaO.SiO ₂	M.P. 1900° C.	Congruently melting in a limited ternary field only (Fig. X.40).
2CaO.SiO ₂	M.P. 2130° C.	Congruently melting (Fig. X.35).
3CaO.2SiO ₂	Dissociates 1475° C.	Incongruent over both binary and ternary fields (Fig. X.37).
CaO.SiO ₂	M.P. 1540° C.	Congruently melting.
3Al ₂ O ₃ .2SiO ₂	Dissociates 1810° C.	Incongruent over both binary and ternary fields.
3CaO.Al ₂ O ₃	Dissociates 1535° C.	Incongruent over both binary and ternary fields.
5CaO.3Al ₂ O ₃	M.P. 1455° C.	Congruently melting.
CaO.Al ₂ O ₃	M.P. 1600° C.	Congruently melting in binary field but only over a limited ternary field (Fig. X.36).
3CaO.5Al ₂ O ₃	M.P. 1720° C.	Congruently melting.

¹ Rankin, G. A. and Wright, F. E., *Amer. J. Sci.*, 39, 52, 1915.



BINARY POINTS			TERNARY POINTS		
1	1800 °C.	P	a	1345 °C	P
2	1545	E	b	1170	E
3	1436	E	c	1265	E
4	1455	E	d	1310	E
5	1475	P	e	1335	P
6	2065	E	f	1380	E
7	1535	P	g	1475	P
			h	1450	P
			i	1360 °C	P
			j	1505	P
			k	1335	E
			l	1335	P
			m	1900	P
			n	1470	P
			o	1512	E
E — EUTECTIC			P — PERITECTIC		

FIG. X.50. THE PHASE DIAGRAM OF LIME-ALUMINA-SILICA



BINARY POINTS			TERNARY POINTS		
1	1810 °C.	P	a	1050 °C	E
2	1545	E	b	1104	P
3	789	E	c	740	E
4	837	E	d	732	E
5	1022	E	e	1063	E
			f	760 °C.	E
			g	1270	P
			h	915	P
			i	955	P
E – EUTECTIC			P – PERITECTIC		

FIG. X.51. THE PHASE DIAGRAM OF SODA-ALUMINA-SILICA

Ternary Compounds

$2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ M.P. 1590°C . Congruently melting (Fig. X.42).
(gehlenite)

$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ M.P. 1550°C . Congruently melting.
(anorthite)

The lowest temperature at which liquid can be present is 1170°C . corresponding to a mixture of 23 parts CaO , 15 parts Al_2O_3 , 62 parts SiO_2 .

The **soda-alumina-silica** system has been studied by Schairer and Bowen¹ and the ternary diagram over the composition range examined is shown in Fig. X.51. The compounds which form are as follows:

Binary Compounds.

$2\text{Na}_2\text{O} \cdot \text{SiO}_2$	—	Probably incongruently melting in both binary and ternary fields, dissociates about 1400°C .
$\text{Na}_2\text{O} \cdot \text{SiO}_2$	M.P. 1089°C .	Congruently melting.
$\text{Na}_2\text{O} \cdot 2\text{SiO}_2$	M.P. 874°C .	Congruently melting.
$3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	Dissociates at 1810°C .	Incongruently melting in both binary and ternary fields.
$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3$	—	Not examined.

Ternary Compounds.

$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ M.P. 1118°C . Congruently melting.
(albite)

$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ M.P. 1526°C . Probably congruently melting.
(carnegieite,
nephelite)

The lowest temperature at which liquid can be present is 732°C . corresponding to a mixture of 26 parts Na_2O , 13 parts Al_2O_3 , 61 parts SiO_2 .

The **potash-alumina-silica** system has also been studied by Schairer and Bowen² and the diagram (Fig. X.52) is similar to that of the soda-alumina-silica system. The ternary compound $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ (orthoclase feldspar), however, melts incongruently except in a limited field of composition (Fig. X.43). A further ternary compound $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ (leucite) is also formed and this melts congruently at 1686°C . The lowest temperature at which liquid can be present is 695°C . corresponding to a mixture of 30 parts K_2O , 4 parts Al_2O_3 , 66 parts SiO_2 .

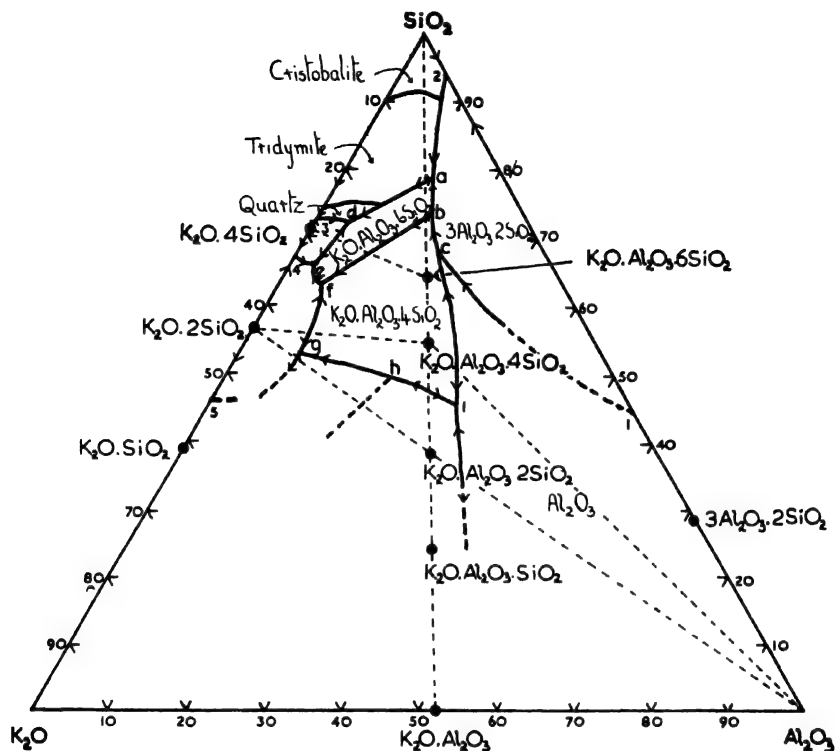
Ternary mixtures within the components **magnesia-lime-alumina-iron oxide-chromic oxide-silica** have been extensively studied because of their importance in the manufacture of basic refractories and the changes which occur in them when used in contact with basic slags.

An excellent summary of the complex phase relationships in these systems has been given by E. F. Osborn.³ Fig. X.53, illustrates a part of the CaO-MgO-SiO_2

¹ Schairer, J. F. and Bowen, N. L., *Amer. J. Sci.*, **245**, 196, 1947.

² Schairer, J. F. and Bowen, N. L., *Amer. J. Sci.*, **245**, 196, 1947.

³ Osborn, E. F., American Iron and Steel Institute, Technical Meeting, October 1954.



COMPOUNDS		POINTS			
BINARY	TERNARY	BINARY		TERNARY	
$3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	$\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$	1 1810 °C	P	a 985 °C	E
mullite diss 1810	felspar diss 1100	2 1545	E	b 1140	P
$\text{K}_2\text{O} \cdot 4\text{SiO}_2$	$\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$	3 769	E	c 1315	P
m.pt. 770	leucite m.pt. 1686	4 742	E	d 710	E
$\text{K}_2\text{O} \cdot 2\text{SiO}_2$	$\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	5 780	E?	e 695	E
m.pt. 1045	kaliophilite 1730			f 810	P
$\text{K}_2\text{O} \cdot \text{SiO}_2$	$\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$			g 905	E
m pt 976				h 1540	P
$\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3$				i 1553	E
m pt ?					
		E – EUTECTIC P – PERITECTIC			

FIG. X.52. THE PHASE DIAGRAM OF POTASH-ALUMINA-SILICA

system within the conjugation triangle of the compounds $\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$ (diopside), $2\text{MgO} \cdot \text{SiO}_2$ (forsterite) and SiO_2 . The phase conditions represent the case of a binary compound, $\text{MgO} \cdot \text{SiO}_2$ which is not stable to its melting point and which forms a series of solid solutions with the third component, diopside. These solid solutions which have the general formula $x\text{MgO} \cdot \text{SiO}_2 \cdot y\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$ are known as the *pyroxenes*. The crystallisation paths of such mixtures have been outlined on page 602 (Fig. X.49).

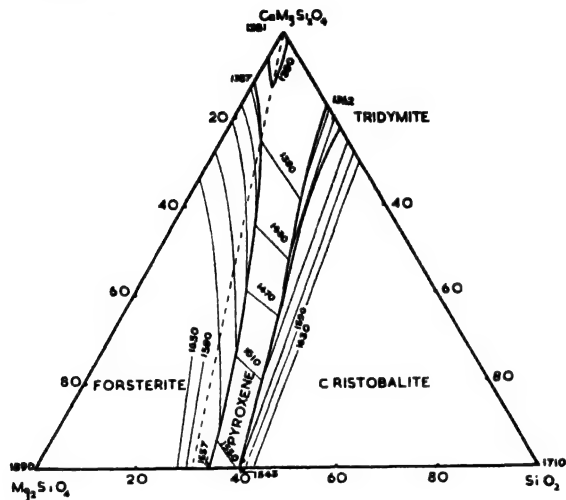


FIG. X.53. THE PARTIAL PHASE DIAGRAM OF LIME-MAGNESIA-SILICA SHOWING THE RELATIONSHIP OF THE PYROXENES

QUATERNARY AND MULTI-COMPONENT SYSTEMS

As the number of components in a system is increased the possible equilibrium conditions extend rapidly. It has been shown that ternary representation requires three binary systems to be translated into three dimensions and that increasing the components to four involves no less than four ternary and six binary systems combined together.

Because of the difficulty of representation when so many components are present, it is best wherever possible to consider multi-component systems as partial systems with congruent compounds represented as components. Thus, for example, the important $\text{MgO}-\text{CaO}-\text{FeO}-\text{SiO}_2$ system which has been investigated in detail by Osborn and Schairer¹ may, over much of the composition range, be studied as partial ternary or binary systems.

Quaternary systems and even those with a higher number of components can, however, be graphically constructed. For example, the component-composition in a quaternary mixture may be represented along the four edges of an *equilateral tetrahedron*. Each corner corresponds to 100 per cent of one component and, thus,

¹ Schairer, J. F. and Osborn, E. F., *J. Amer. Ceram. Soc.*, 33, 160, 1950.

the composition of any four-component mixture can be fully described by such a spacial model (Fig. X.54). There is no axis available for temperature representation, but usually it is indicated by three-dimensional isotherms or more simply by arrows on phase boundary curves, pointing in the direction of falling temperature.

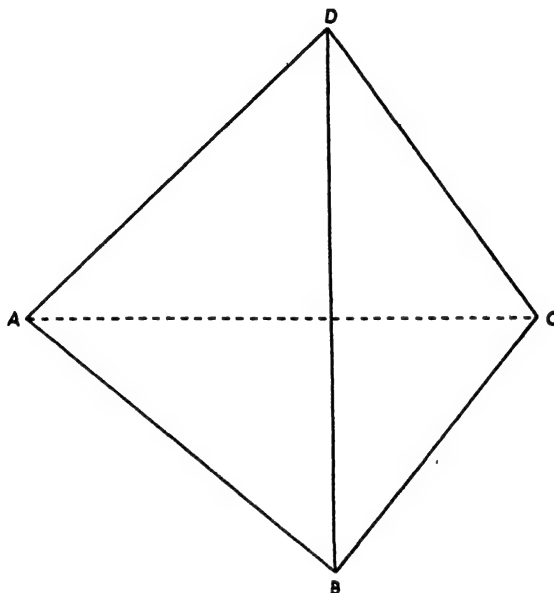


FIG. X.54. THE EQUILATERAL TETRAHEDRON FOR REPRESENTING THE COMPOSITIONS OF QUATERNARY MIXTURES

EXPERIMENTAL METHODS FOR THE DETERMINATION OF EQUILIBRIUM DIAGRAMS

Equilibrium implies that all reactions between the components of any mixture have proceeded to completion under the specific experimental conditions and that no further change would take place in the products if the same conditions were maintained for an infinite period of time. Reactions between solid components are frequently very slow, particularly where the rates of diffusion are low, as in many silicate mixtures. Consequently, it is doubtful whether equilibrium conditions would be reached, in many instances, in the periods of time feasible for laboratory experimentation; the simple heating of mixed components to specific temperatures, even for long periods, is insufficient to reach equilibrium in many ceramic systems. **Heating Curves.** In metallurgical practice the appearance of a phase in a certain mixture is so rapid (sometimes instantaneous) that a *thermal arrest* can be detected at a well-defined temperature on either a heating or a cooling curve. This is produced by the changes in latent heat which accompany the melting or crystallisation of phases. Phase boundary lines can be established with certainty and there is no

necessity to identify the equilibrium products in a wide range of mixtures in order to derive the complete equilibrium diagram.

Ceramic mixtures do not, however, readily lend themselves to such treatment. Crystal phases form too slowly to produce a pronounced 'arrest' and *super-cooling* is a common phenomenon. Silicate melts can often be cooled to a temperature well below that at which a solid phase should appear without any crystallisation taking place.

Quenching Methods. When silicate systems are being studied another very troublesome feature is that a glassy phase is easily formed and it may persist and crystallise only with difficulty even under prolonged conditions of test. Hence the determinations of phase equilibrium diagrams for ceramic systems require special techniques; the most widely used of which is that described by Morey.¹ The finely-divided components are intimately mixed in known proportions and then fired in suitable containers to the desired temperature. After prolonged, carefully controlled soaking, the samples are instantaneously quenched to room temperature in a suitable liquid. This usually has the effect of *freezing* the phases which were present at the temperature of the test and thus they may be identified and often estimated by suitable methods (see Chapter V). It is advisable to ensure that true equilibrium has been reached by regrinding the quenched specimen and again heating and soaking it at the same temperature. If after requeenching, the phases have not been materially altered, equilibrium may be assumed; otherwise, further treatment is necessary.

If tests are being carried out at temperatures where little or no liquid can form, considerable time may be saved by first heating the mixed components to a temperature in excess of that at which the phase determination is to be made. The mass will react more rapidly and become more uniform and thereby reach equilibrium at the desired temperature more rapidly than would otherwise be the case.

A quenched body will show crystals developed at the temperature of soaking and also a glassy, homogeneous phase which has been formed from any liquid present in the heated mass. A microscopic examination in conjunction with X-ray analysis are the most valuable methods of phase identification, although others may be used with advantage in some instances.

Should any crystal phase have a rapid transition at temperatures below that of the test, obviously, quenching may give misleading results; it is usually possible, however, to make allowance for such changes and, if the mechanism of transition is known, to deduce how much of the original phase was present.

The establishment of phase boundary lines by this method is a comparatively simple matter. If the same mixture of components is soaked at a series of ever-increasing temperatures and the phases present at each stage are carefully assessed, the range of stability of each crystal form can be established. Similar experiments may be carried out, using mixtures of different compositions and phase boundary lines can be constructed for the whole diagram.

When the components form solid solutions, the determination of the phases is greatly complicated. In most cases neither microscopic nor X-ray determinations are adequate to indicate the composition of the solid solution and it is usually necessary to separate the phases and to analyse each individually.

¹ Morey, G. W., *J. Wash. Acad. Sci.*, 13, 325, 1923.

Studies of Model Systems. Silicate mixtures and other compositions of interest to ceramists melt only at high temperatures where the difficulties of observation and measurement are very great. Goldschmidt¹ has shown that similar phase relationships exist between some fluorides and oxides, but the changes in the fluorides take place at much lower temperatures, and can thus be studied more conveniently.

The fluoride ion is of similar size to oxygen but is of unit charge. Monovalent cations form fluorides which have a similar structure and properties to oxides of divalent cations of the same size, but, because the bonding between monovalent ions is much weaker than between divalent ions, the melting point is correspondingly lower (see p. 639). Table X.VI shows the equivalent fluoride and oxide compounds and their melting points.

TABLE X—VI. THE MELTING POINTS OF SOME OXIDES AND THEIR CORRESPONDING FLUORIDE MODELS

Fluoride	Cation Size Å	Melting Point °C.	Melting Point K°*	Oxide	Cation Size Å	Melting Point °C.	Melting Point K°*	$\frac{T_o}{T_f}$
LiF	0.60	870	1143	MgO and ZnO	0.65 0.74	2820 1975	3093 2248	2.71 1.97
NaF	0.95	988	1261	CaO	0.99	2572	2845	2.25
KF	1.33	846	1119	BaO	1.35	1923	2196	1.96
BeF ₂	0.31	543	816	SiO ₂	0.41	1728	2001	2.45
MgF ₂	0.65	1240	1513	TiO ₂	0.68	1825	2098	1.39
CaF ₂	0.99	1330	1603	ZrO ₂ and ThO ₂	0.80 1.02	2720 2800	2993 3073	1.87 1.91

* K° indicates absolute temperature.

The relationship between the absolute temperature (K°) of melting of the oxides and the corresponding fluoride is about 2 to 1, as shown by the last column in the Table.

Provided that the limitations of model systems are appreciated, their study often reveals much valuable information of the equilibria relationship of high melting point oxides.

The **lithium fluoride-sodium fluoride** mixture is very similar to the **calcium oxide-magnesium oxide** system; a eutectic is formed in both which corresponds in composition to about 40 per cent molecular ratio of the lower melting component. The similarity between the **lithium fluoride-beryllium fluoride**² and the **zinc oxide-silica** mixtures is shown in Fig. X.55 A and B. The liquidus curves are remarkably similar but the compound Li₂BeF₄ which resembles Zn₂SiO₄ (willemite) dissociates at temperatures below that of the eutectic. The study of the model system **calcium fluoride-beryllium fluoride** enabled the phase relationships in **thoria-silica** mixtures to be predicted.³

¹ Goldschmidt, V. M., *Skr. Nor. Videnskaps-Akad.*, Oslo 1, *Mat-Naturv. Klasse*, 8, 7, 1927.

² Roy, D. M., Roy, R. and Osborn, E. F., *J. Amer. Ceram. Soc.*, 37, 300, 1954.

³ Roy, D. M., Roy, R. and Osborn, E. F., *J. Amer. Ceram. Soc.*, 36, 185, 1953.

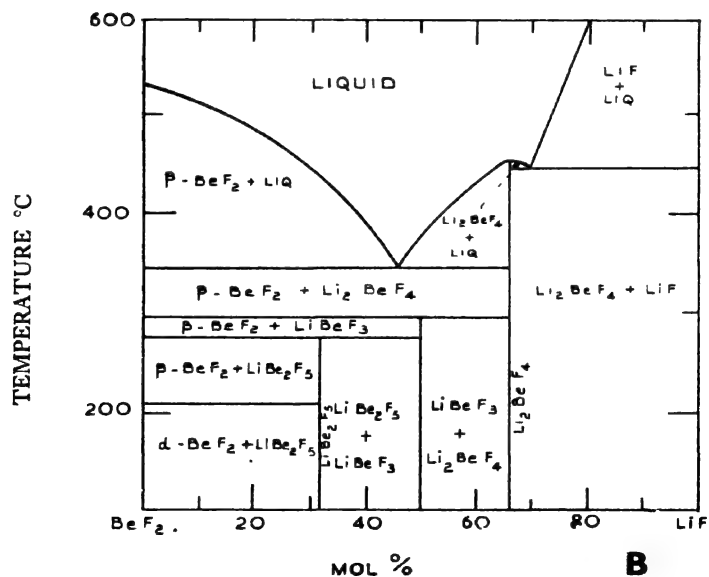
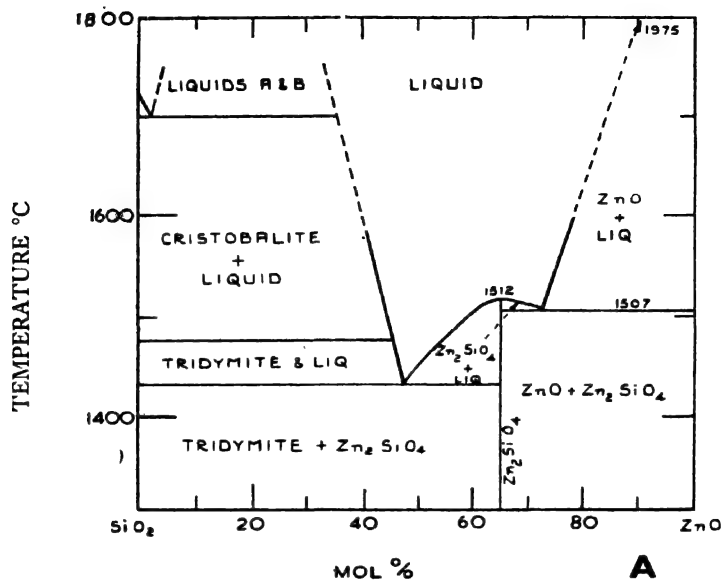


FIG. X.55. A COMPARISON OF (A) THE ZINC OXIDE-SILICA PHASE DIAGRAM AND (B) ITS FLUORIDE MODEL, THE LITHIUM FLUORIDE-BERYLLIUM FLUORIDE DIAGRAM

An excellent survey of the value and use of fluoride models in equilibrium studies of refractory oxides has been compiled by E. F. Osborn.¹

THE IMPORTANCE OF EQUILIBRIUM DIAGRAMS IN CERAMIC STUDIES

ALTHOUGH it is undoubtedly a fact that most ceramic bodies do not reach equilibrium under normal manufacturing conditions, equilibrium diagrams are of very great value and increasing use is being made of the information they contain. They must be used with care, however, because—in addition to rarely attaining equilibrium in practice—raw materials are often too impure to be regarded as simple mixtures of components. Despite serious objections of this nature, if due precautions are taken, important deductions can be made from equilibrium studies even of highly complex mixtures.

Equilibrium diagrams are valuable for:

1. Predicting the changes which are liable to occur in a body on prolonged firing.
2. Indicating the lowest temperature at which liquid will be found in a mixture of components and also the amount of such liquid.
3. Determining the nature of the bond in a fired ceramic material or article, i.e. whether it is glassy or crystalline.
4. Suggesting the approximate refractoriness or melting point of the body.

Much information has been derived from a study of equilibrium diagrams in systems which are mainly liquid at the temperature of firing, such as glass or slags, where the phases present often approach true equilibrium. In silicate systems, for example, good permanent glasses are liable to form in the composition ranges where eutectics with low melting-points or incongruent compounds are formed. Crystal formation and other changes are more liable to occur when there is easy movement of the reacting material and the respective atoms. Silicate melts have a fairly low viscosity at high temperatures, but this rapidly increases as the temperature is lowered. Hence mixtures which cannot contain solid phases until the temperature is low, will virtually freeze and prevent crystal formation. The formation of incongruent compounds always implies a change which takes place largely in the solid state. Diffusion reactions of this type are invariably slow and are easily suppressed if the viscosity of the system is high and the cooling relatively rapid.

THE VELOCITY OF REACTIONS AND CHEMICAL KINETICS

ALTHOUGH equilibrium studies on ceramic materials have been actively pursued only in comparatively recent years, even less attention has been devoted to the speed or rate at which such reactions occur. This subject is termed *chemical kinetics* and although the processes or reactions in many gaseous or solution systems have been deduced, the fundamental mechanisms of solid transformations are not well established.

¹ Osborn, E. F., *Ceram. Age*, 60, 41, 1952.

Some reactions proceed so rapidly that they are explosive in character, whilst others change at a rate undetectable by normal methods of measurement. Many oxidation reactions such as those of sulphur and carbon in the presence of potassium nitrate are complete in a fraction of a second, but the change from cristobalite to quartz at low temperatures is so slow that it requires a geological age for completion.

The velocity with which a reaction proceeds is of great importance, particularly in ceramic studies, where the end-product of a firing cycle has so pronounced an influence on the properties. Chemical reactions which are complete at equilibrium-firing may be only partially so under normal operating conditions and the composition of the product may bear no relation to that predicted by equilibrium studies.

It is known that the velocity of a reaction is dependent mainly on the temperature and on the concentration and affinity of the reactants, although when one or more of the reactants are solid a third factor, *availability* or *contact-area* must also be included.

REACTIONS BETWEEN GASES AND LIQUIDS

ARRHENIUS¹ was the first to recognise that reactions which took place entirely in the gaseous or liquid phase depended on the collision-frequency of reacting molecules, atoms or ions. If this were the only factor involved, the reaction rate would depend only on the concentration, for this would determine the number of collisions in a given time. Arrhenius therefore concluded that some molecules in a gas must be more 'activated' and are able to react more readily when they come into contact with others. These 'active' molecules may be considered to have a higher kinetic energy than the average. On this basis, the reaction rate for different types of *gaseous reactions* may be predicted as depending on the number of molecules which take part in the change.

First Order Reactions. When only one molecular type is involved in the change, the rate of reaction must be proportional to its concentration at any time. Supposing for example, the reaction is of the type $A \rightarrow B + C$ (as in decomposition reactions), the rate of reaction $-(dc/dt)$ will be directly proportional to the concentration (c) of the reactant A at that particular time; thus

$$\frac{-dc}{dt} = kc \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where k is a constant depending on the collision rate of 'active' molecules. It is known as the *rate constant*. Simple integration of this expression gives:

$$\ln c = -kt \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\text{or } c = C_0 e^{-k(t-t_0)} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where C_0 is the initial concentration at time t_0 .

Equation (2) predicts that, if the reaction is first order or unimolecular, the concentration of the reactant will fall logarithmically with respect to time.

¹ Arrhenius, *Z. physik. Chem.*, 4, 226, 1899.

Second Order Reactions. If two molecules are involved in a reaction then it is of *second order* and is of the type:



The rate of such a reaction will depend on the relative concentrations of both the reactants and these will each decrease at the same rate and the rate of reaction may be expressed as:

$$\frac{-dC_A}{dt} = \frac{-dC_B}{dt} = kC_A \cdot C_B$$

where C_A and C_B are the respective concentrations of components A and B at time t .

If

$$C_A = C_B = c$$

then

$$\frac{-dc}{dt} = kc^2 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

By integration

$$\frac{1}{c} = kt \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Therefore in *bimolecular* or *second order reactions* the concentration of reactants varies inversely with time.

Third Order Reactions. Reactions between three components are known although they are rare. The rate may be predicted by similar reasoning as:

$$\frac{-dc}{dt} = c^3 \quad \text{if } C_A = C_B = C_C = c \quad . \quad . \quad . \quad (6)$$

Such simple behaviour may be complicated by reverse, side or consecutive reactions which may be simple in themselves, but, when taken together, may give rise to a complex rate expression, unless one stage predominates or is *rate determining*.

Temperature also has a pronounced influence on the reaction rate and is contained in the rate-constant k to which it is related by the expression:

$$k = Ae^{-E/R/T} \quad . \quad . \quad . \quad . \quad (7)$$

where E is the energy of activation, R is the gas constant, T is the absolute temperature and A is a constant containing an entropy term. Thus, if the value of k for a particular reaction can be determined at several temperatures, the activation energy of that reaction (E) is given by the slope of a graph of $\ln k$ against $1/T^\circ A$ because, from equation (7):

$$\ln k = \frac{-E}{RT} + \ln A \quad . \quad . \quad . \quad (8)$$

The simple kinetical equations derived in the previous sections apply only to gaseous or liquid reactions where the individual molecules are capable of free movement and reactions proceed mainly through collisions. The molecular energy term is predominantly that of *translation*.

REACTIONS INVOLVING SOLID SUBSTANCES

WHEN reactions involving solid phases are considered, the individual reacting units of atoms or ions are rigidly held within a crystal lattice and, consequently, before a rearrangement can take place the equilibrium lattice positions have to be disturbed. Consequently *vibrational* movement of the bonds becomes the dominant factor and reaction can occur only when this has exceeded a certain amount. Even when sufficient energy is available to break bonds, the released units (unless they are gaseous), have no freedom of movement, but can only transfer to an adjacent lattice-site. Such reactions can proceed only through the mechanism of *diffusion*.

Reactions in the solid state are, consequently, slow, but they nevertheless proceed with finite velocities. For example, pure kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), will not form a liquid phase below 1545°C ., yet at considerably lower temperatures, mullite and cristobalite are formed from it.

The kinetical mechanism of most reactions involving solids is difficult to derive because the *rate-determining factor* is not always obvious.

In a simple liquid reaction, such as $\text{CaCl}_2 + \text{Na}_2\text{CO}_3 = \text{CaCO}_3 + 2\text{NaCl}$ the reaction rate is governed by the rate of formation of insoluble CaCO_3 .

In the decomposition of calcium carbonate



the partial pressure of CO_2 over the reactants is the rate-determining factor.

In most solid state changes, no such obvious governing mechanism is present, as for example in the reaction



which proceeds appreciably at 774°C . although at that temperature neither barium carbonate nor free silica dissociates or forms a vapour phase.

Some types of solid reaction proceed because the *free energy* of the system is lowered as a consequence. Free energy may be expressed in terms of the lattice or crystal energies of the solid phases. If a decrease in total energy can be brought about by a reaction between the components, that change will tend to take place.

Thus, in the simple alkali halides, sodium chloride reacts with potassium fluoride to give sodium fluoride and potassium chloride because such a reaction involves an energy decrease of about 9,000 cal. per mole.

Thus $\text{NaCl} + \text{KF} = \text{NaF} + \text{KCl} + 9000 \text{ cal. per mole.}$

If the finely-powdered reactants are intimately mixed the reaction proceeds readily. Unfortunately, the lattice energy of crystals is not easy to calculate and the value for only a relatively few simple crystals is known with certainty, but this concept of a thermodynamical basis for solid reactions is valuable.

Solid reactions may be generally classified into two groups (a) internal rearrangements, and (b) external interactions. The first type simply involves a 'change-round' in an existing atomic arrangement at a specific temperature without the introduction of foreign agencies; whilst the latter type implies transference of the atoms or ions of one crystal form across a surface into a lattice of another type. Although these two types are fundamentally different in character the underlying mechanisms and driving forces are similar. In each case, atoms or ions must leave

their original lattice-sites and transfer to vacant positions in the immediate vicinity. As would be expected, the type of lattice determines the relative ease of such a transfer; massive, tightly-packed structures are not conducive to ionic movements, but spongy, cellular and framework structures are particularly adaptable to the process of *diffusion*.

(a) **Internal Rearrangement Reactions.** When no atomic or ionic material crosses the crystal boundaries, yet a reaction takes place at a certain temperature, the chemical composition of the initial and final states must be the same. Such reactions are termed *polymorphic transformations* and two clearly defined types are recognised:

1. The first involves a slight rearrangement and an alteration in the degree of order or symmetry of the crystal. No bonds within the crystal are broken; only a spacial reorientation of adjacent atoms occurs. Little or no heat is involved in the transformation, but the specific heats of the initial and final states may be substantially different. The reaction takes place at a clearly defined temperature and is instantaneously reversible. This type of change is known as an *order-disorder change* and is typified by the various silica *inversions*. In these cases, the lattice of the β - or high temperature modification is of the highest symmetry but, on cooling, the contraction is so great that the angles between linkages cannot be maintained. The change from β - to α -quartz is considered to involve only a change in the —Si—O—Si— bond angle from 180° , although in cristobalite and tridymite a rotational movement may also occur (see Chapter III). The heat change in every case is small, being of the order of 3–6 calories per mole.

2. A second type of internal rearrangement reaction requires a migration of atoms or groupings and a disruption and re-forming of bond linkages. The final state has a completely different structure and symmetry system. The reaction involves a considerable energy change and although a definite temperature can be defined below which the transformation cannot proceed, the reaction, even well above this critical point is often sluggish. In contrast to the order-disorder type of change, the reverse reaction below the critical point is also slow and may require a geological age for completion. Changes in silica minerals also illustrate this type of reaction but, in this case, the *conversions* provide the example. Thus, quartz with a pseudo-hexagonal lattice converts to cristobalite with a cubic lattice, or to tridymite which is tetragonal, at temperatures above 870°C . The energy change, in each case, is comparatively high being of the order of 6,000 cal. per mole.¹ Fig. X.56 is an idealised picture of the structural difference between the two types of polymorphic transformations. The order-disorder inversion (a) involves only a bond angle change, the conversion reaction (b) changes the atomic arrangement completely.

Changes of the latter type, although producing a complete alteration of structure, involve little migrational or translatory movement of atoms or ions. The structure may simply glide or twist about an axis, or ions may migrate along a channel in the framework structure in such a way that crystal discontinuities do not arise. The change from meta-kaolinite to mullite could be considered as of this type. At temperatures above about $1,000^\circ\text{C}$., the silicon ions or silica groupings (SiO_4)⁴⁻ partly migrate and take up other positions around the octahedral alumina layers which remain virtually unchanged spacially throughout the reaction.

¹ Bernal, J., *Trans. Farad. Soc.*, 34, 6, 1938.

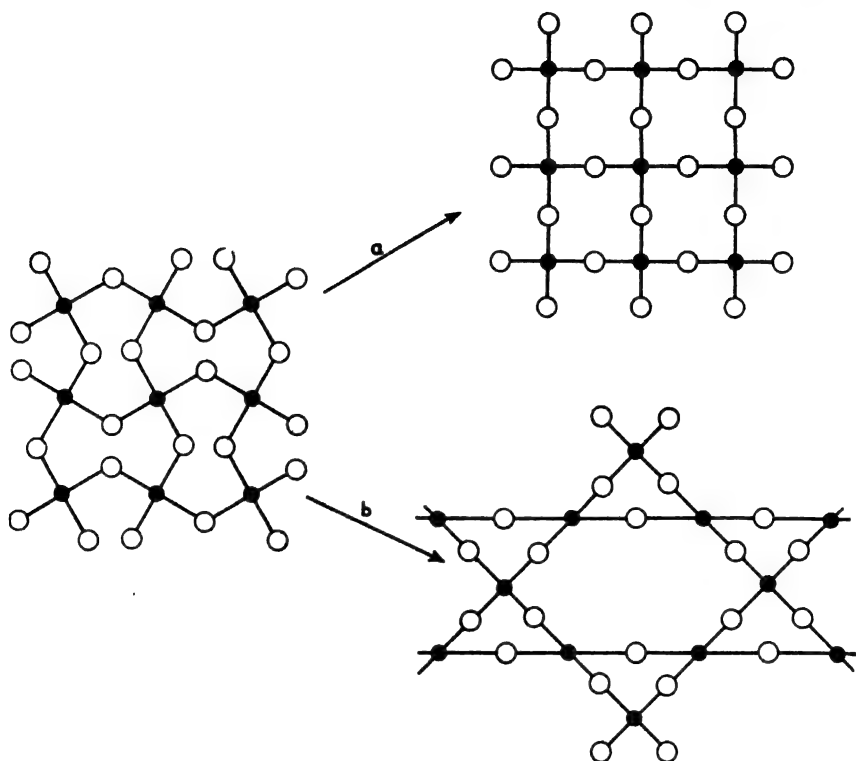


FIG. X.56. AN IDEALISED REPRESENTATION OF THE DIFFERENCE BETWEEN
(a) THE INVERSION; AND (b) CONVERSION REACTIONS

(b) **External Interactions.** When two unlike materials are in contact and reaction occurs, the transfer of ions across the adjacent surfaces proceeds by a mechanism similar to that involved in the rearrangement of ions in polymorphic transformations. Ions transfer to vacant lattice-sites across the contact-surfaces in such a way that only a minimum translatory movement is involved. If the opposing crystal lattices are close-packed, little migration is possible and ionic transference will usually be towards the medium containing the maximum vacant lattice-positions or the more open structure.

Reactions between two or more solid substances are of two general types as follows:

(a) Additive—where $A + B = AB$

and the compound AB forms a separate phase, or

(b) Exchange—where $A + BC = AC + B$

or

$AB + CD = AD + CB$

The mechanism is similar in both cases, i.e. *diffusion*.

MECHANISM OF DIFFUSION REACTIONS

THE physical mechanism of diffusion is directly related to the properties of the surfaces in contact. Weyl's suggestion that the outermost layers of atoms in a crystal have insufficient 'screening' and hence must be distorted, has already been demonstrated (p. 418). In these dynamically unstable surface regions there is always the possibility of ionic transference, especially if the vibrational movement is accelerated by heat, or if a suitably receptive surface is brought into close association.

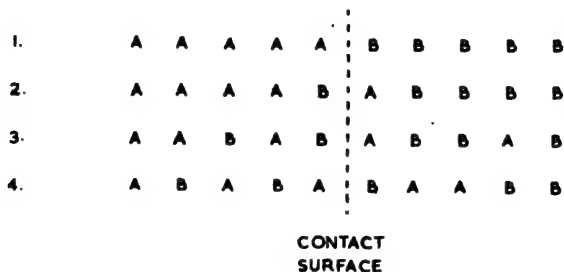


FIG. X.57. A FIGURATIVE REPRESENTATION OF FOUR STAGES IN THE DIFFUSION OF COMPONENTS A AND B ACROSS A CONTACT SURFACE

The mutual diffusion stages of components A and B might be represented as in Fig. X.57, although the individual rates into the opposite medium may not be identical. There is, however, another factor which has an important bearing on the rate of diffusion reactions. Defects are common in crystal lattices and these facilitate the rate of transfer of ions. Schottky and Wagner have calculated that in any crystal lattice at temperatures above absolute zero, a definite number of ions will have left their normal sites and be occupying positions of disorder. Defects of this type do not occur on a large scale—perhaps not more than one ion in 100,000 will be out of place—yet this is sufficient to permit diffusion.

Four distinct possibilities of *defect structures* are recognised and these are illustrated in Fig. X.58.

The important cases are: (a) where one type of ion transfers to an interstitial position; this is known as *Frenkel disorder*; and (c) where lattice holes are formed; this is called *Schottky disorder*.

Frenkel disorders are more likely to occur when the anion and cation differ substantially in size and where polarisation (see Chapter II) is very strong as, for example, in silver chloride and bromide.

Schottky disorders occur when the ions are of similar size and the polarisation is weak, as in the alkali halides.

The number of lattice imperfections in a crystal depends on the temperature, hence the diffusion rate increases likewise.

Although diffusion proceeds through the transference of ions through defects in a crystal or through the spaces in an open-structured lattice, the detailed mechanism is a matter for conjecture.

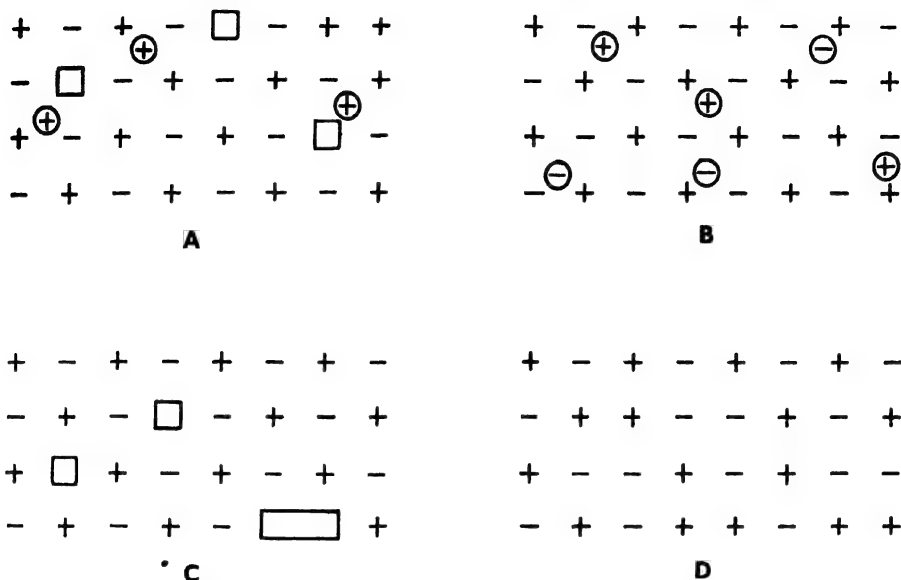
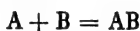


FIG. X.58. FOUR TYPES OF DEFECTS IN CRYSTAL LATTICES

A The transfer of ions to interstitial lattice positions; B the inclusion of both anions and cations in interstitial lattice positions; C vacant lattice sites; and D inverted ionic positions

Jander¹ suggests that the reaction



proceeds in stages as illustrated in Fig. X.59.

A weak bond between the reactive components A and B is first formed at contact surfaces (stage 1). Mutual ionic transfer coupled with bonding in the surface layer then proceeds (stage 2) until a coherent layer of compound is formed (stage 3). The final phase involves molecular development (stage 4) inside the crystal which eventually resolves into an ordered crystal lattice (stage 5). Diffusion proceeds through the agency of a layer of product which migrates away from the surface. The nature of the product or diffusion layer may not correspond to the final product, but may be of an intermediate or transitory character.²

The Nature of Diffusion Layers. Although it is well established that diffusion reactions propagate through an advancing interface, the true nature of this 'diffusion layer' can only be surmised. It may be that the condition in such regions is a random distribution of diffusing ions which distort the original structure, until eventually a new crystal phase will form which Jander has termed a *hybrid compound* and other authorities have referred to a *transitional form*. Diffusion proceeds more rapidly between two components under conditions where unstable compounds are more liable to form, although this generalisation cannot be carried too far.

¹ Jander, W., *Z. Angew. Chem.*, 49, 88, 1936.

² Hedvall, J. A. and Sjoman, P., *Z. Electrochem.*, 37, 130, 1931.

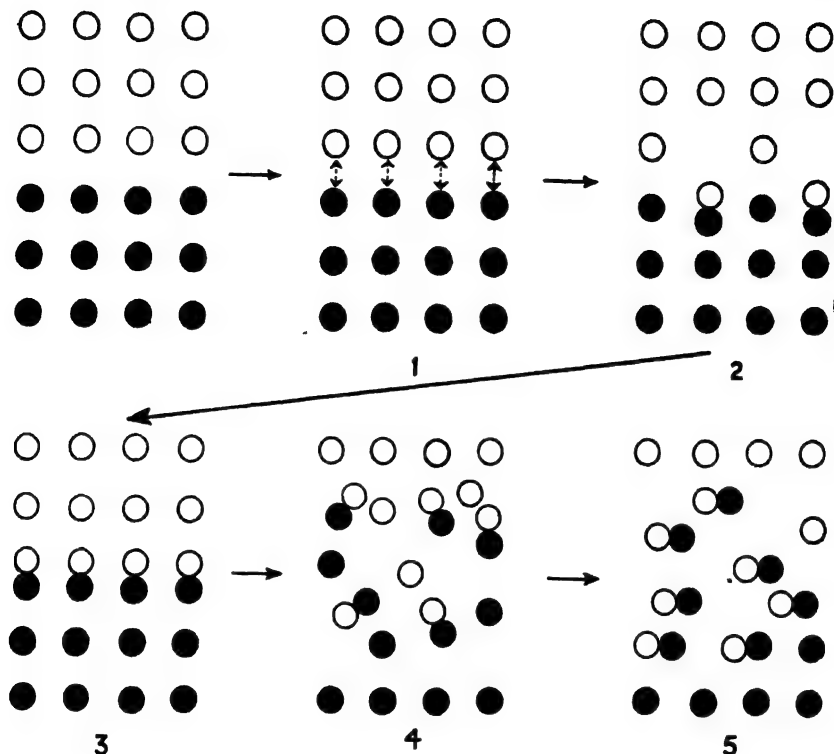


FIG. X.59. STAGES IN THE DEVELOPMENT OF A DIFFUSION REACTION

Solid reactions commence at points of contact of opposite components. Hence, the 'active' concentration of reactants in such places will depend on their relative diffusion rates and may not be related to the overall ratio in which they are mixed. Jander has shown, for example, that in a mixture of silica and calcium oxide the first product of solid reaction is always the orthosilicate and it is only after prolonged heating that the metasilicate may form. Tricalcium silicate also appears at some stage of the reaction, as shown in Fig. X.60.

The formation of a diffusion layer is dependent on several factors and more than one underlying mechanism is involved. Where one component diffuses into another of different type, the mobility of the transferring ions will be the principal determinant. Therefore the formation and spread of a diffusion layer will depend on the availability of foreign ions and on the ease of transfer through the receptive lattice.

Diffusion proceeds mainly through crystal defects or along channels in a crystal with a framework structure. An increase in temperature will produce more defects and, at the same time, increase the mobility of the diffusing ions. Hence, the rate of diffusion is largely dependent on the temperature of the surroundings. Hedvall has shown that the diffusion rate is also considerably accelerated when the receptive

medium is undergoing a transitional change. Iron oxide, for example, can be induced to enter the quartz lattice with an appreciable velocity at about 573°C . (the inversion temperature); the rate does not increase to any extent above this temperature until the lattice becomes unstable when the conversion to cristobalite commences.

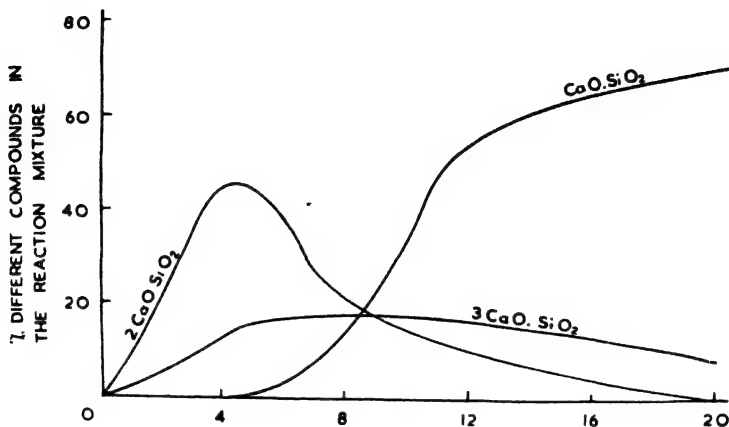


FIG. X.60. THE PRODUCTS OF FIRING LIME-SILICA MIXTURES FOR VARIOUS PERIODS OF TIME AT 1300°C . (after Jander)

An altogether different mechanism of diffusion-layer formation and progression must be dominant in reactions which do not involve ionic transfer. Polymorphic transformation (p. 617) or decomposition reactions require that the linkages between adjacent ions should be altered in direction or completely broken. This can only arise as the result of an increase in the vibrational energy of the lattice which, if it becomes sufficiently large, will permit an ion to move out of the spheres of influence of its immediate counterbalancing neighbours. Here again, an increasing temperature will be an important factor as also will be a defective structure or an open lattice. Weyl has pointed out that the presence of foreign ions in a disturbed lattice may considerably increase the ease of rupture of linkages.

Even in changes which do not involve ionic transfer, the reaction proceeds by the propagation of a diffusion-type layer. At some point or points in the lattice, conditions are more favourable to the commencement of a reaction which then spreads from nuclei of this type throughout the entire mass. This diffusion layer exerts a pronounced influence on the progress of the solid reaction; it may behave as (a) a barrier which slows down the rate, or (b) as an intermediary which propagates at a steady linear rate, or (c) as a catalyst which accelerates the process.

(a) Jander has made a comprehensive analysis of the kinetics of a reaction involving a diffusion barrier and he deduced that, in a cylindrical specimen reacting from one end-face under isothermal conditions, the rate of reaction (dy/dt) was inversely proportional to the thickness (y) of the layer formed, so that:

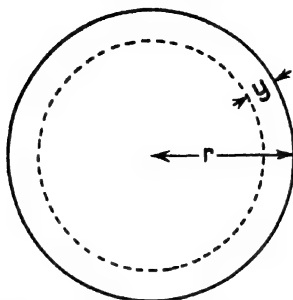


FIG. X.61. THE RATE OF THE PROPAGATION REACTION IN A SPHERE

The relationship between x and the thickness of the reacted layer y is given by:

$$\begin{aligned} \frac{x}{100} &= \frac{\text{volume of original sphere} - \text{volume unchanged after time } t}{\text{volume of original sphere}} \\ &= \frac{\frac{4\pi r^3}{3} - \frac{4\pi(r-y)^3}{3}}{\frac{4\pi r^3}{3}} \\ &= 1 - \frac{(r-y)^3}{r^3} \end{aligned}$$

or

$$\begin{aligned} \frac{(r-y)^3}{r^3} &= \frac{100-x}{100} \\ \frac{r-y}{r} &= \sqrt[3]{\frac{100-x}{100}} \\ \frac{y}{r} &= 1 - \sqrt[3]{\frac{100-x}{100}} \\ y &= r \left(1 - \sqrt[3]{\frac{100-x}{100}} \right) \quad \dots \quad (12) \end{aligned}$$

As y is the distance advanced by the interface in time t , if the reaction is retarded by the diffusion-barrier, equation 9a can be substituted, i.e.

$$y^3 = 2kt \quad (\text{the constant } A \text{ is equal to zero because } y = 0 \text{ when } t = 0)$$

Therefore the expression (12) becomes

$$\begin{aligned} 2kt &= r^3 \left(1 - \sqrt[3]{\frac{100-x}{100}} \right)^3 \\ \text{or} \quad \left(1 - \sqrt[3]{\frac{100-x}{100}} \right)^3 &= \frac{2kt}{r^3} = Kt \quad \dots \quad (13) \end{aligned}$$

The constant K contains the diffusion-coefficient D and is also inversely related to the square of the initial radius of the sphere, or to the surface area factor (surface area of a sphere = $4\pi r^2$).

Equation 13 is a rate expression for it relates the percentage of sphere decomposed in unit time; hence K is, in every sense, a rate-factor, and its value governs the speed of reaction. As in simple gas reactions (p. 615), K is related to absolute temperature (T) by the standard Arrhenius equation

$$K = Ae^{-E/RT}$$

where R is the gas constant; A is a constant depending on the ease of diffusion, the number of mobile particles and the physical state of the material; and E is a term which expresses the energy required to activate a gram-molecule of particles so that they can move between points in the lattice; in other words, E is the *energy of activation*.

The general equation (13) expressing the rate of a reaction in a sphere is of general application. It describes the conditions under which a solid sphere will dissolve in a surrounding liquid or slag, provided that the diffusing layer behaves as a barrier or retarder to the progress of the reaction.

When the reaction layer transmits the reaction at constant velocity and neither retards or catalyses the rate of transfer (as in case (b) page 623), equation (10a) must be substituted in the expression

$$y = r \left(1 - \sqrt[3]{\frac{100 - x}{100}} \right)$$

Then

$$1 - \sqrt[3]{\frac{100 - x}{100}} = \frac{kt}{r} \quad (14)$$

k is usually termed the *linear rate of propagation* and is given the conventional symbol μ . This equation may be expressed in another form as

$$1 - a = \left(1 - \frac{ut}{r} \right)^3$$

where a is the proportion of material reacted in time t , which, when completely expanded, is

$$1 - a = 1 - \frac{3ut}{r} + \frac{3(ut)^2}{r^2} - \frac{(ut)^3}{r^3}$$

To a first approximation, this expression may be regarded as the expansion of the equation:

$$1 - a = e^{-\frac{3ut}{r}}$$

or

$$\ln(1 - a) = \frac{-3u \cdot t}{r} \quad (14a)$$

Now a is the proportion of material which has reacted in time t so if α is the proportion of original material remaining then

$$\ln \alpha = \frac{-3u \cdot t}{r} \quad . \quad . \quad . \quad . \quad (14b)$$

This last equation has the form of a first order equation (p. 614) where $3u/r$ is equivalent to the rate constant k .

Similar equations can be derived for particles of other shapes and where the diffusion mechanism is of one of the three general types as outlined on p. 623.

The Nucleation Rate. In the diffusion reactions, so far considered, only the rate of propagation of an interface has been derived, but the rate at which such a layer is initially formed is of equal importance.

If two solid substances react, they can do so only at those surface areas which are in contact. The reaction must be initiated by the transfer of atoms or ions of one type over the surface layers of both phases and into the lattice of the other component. It is to be expected that the energy required and the mechanism of such transfer will be dissimilar from the propagation of foreign ions which have already been incorporated in another lattice.

Diffusion proceeds by the transfer of ions from a lattice-site into a defect or vacant position elsewhere in either the same crystal or in an entirely different crystal. Defects in lattices are limited and occur mainly in surface layers (p. 619), hence, if two crystals are in contact and a defect or 'activation centre' in one component is in close proximity to a receptive condition in the other, transference of one phase into another can proceed. A reaction will commence, therefore, at nuclei on the surface and will then radiate by normal diffusion until a complete interface is formed as shown in Fig. X.62. The first diagram (A) shows two contact surfaces with defect points; the second (B) shows several nucleated areas which spread with a spherical interface; and the third (C) shows how several such points may merge to form a linear interface.

Some reactions, involving a polymorphic change without requiring any transference of ions across a contact surface, can also commence on a surface defect which nucleates readily and then merges with others to form a continuous interface, as in the conversion of pure quartz which is discussed more fully in a later section.

The rate of formation of nuclei is governed by the normal probability law as follows:

$$n_t = n_0 e^{-kt} \quad . \quad . \quad . \quad . \quad (15)$$

where n_0 and n_t are respectively the total number of possible activation centres and the number which remain after time t , and k is a constant, equivalent in all respects to a normal rate constant.

If it is assumed that the process of nucleation involves an appreciable molecular change, as often appears to be the case, and α is the percentage of the original phase remaining after time t

$$\alpha = e^{-kt} \quad . \quad . \quad . \quad . \quad (15a)$$

or

$$\ln \alpha = -kt \quad . \quad . \quad . \quad . \quad (15b)$$

Thus the rate of a purely nucleation reaction has a form equivalent to that of a first order reaction (p. 614).

Obviously, the number of nucleation spots will influence the reaction rate, hence if surface defects are the main cause, the rate will be proportional to the surface area of the reacting particles.

The rate of nucleation (k) is also dependent on temperature and related by the Arrhenius equation (p. 615):

$$k = Ae^{-E_N/RT}$$

where E_N is the *energy of nucleation*.

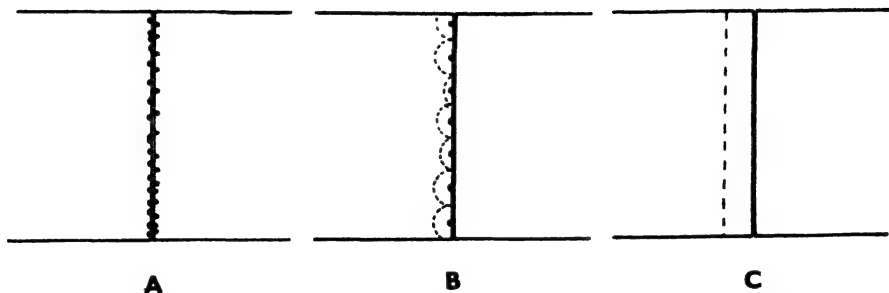


FIG. X.62. THE PROGRESS OF A SOLID REACTION WHICH PROCEEDS ACROSS AN INTERFACE

A Defect points in the surface layers; B the formation of nucleated areas;
and C the formation of a linear reaction layer

Relationship between the Nucleation and Propagation Rates in Solid Reactions. Solid reactions may be divided into two stages (*a*) *nucleation*—when mainly surface defects are being nucleated, and (*b*) *propagation*—when such nucleated regions spread by normal lattice diffusion through the mass of the material. The form of reaction can be mathematically deduced and the rate at which each stage proceeds is governed by constant terms which are known respectively as (*a*) *the nucleation constant* (see equation 15b), and (*b*) *the propagation constant* (see equations 13 and 14).

The complete form of the solid reaction depends entirely on the relative magnitudes of these two terms and, if one greatly exceeds the other, it will be the predominant mechanism. There are three important cases:

1. Where the nucleation rate is rapid, but the rate of propagation is slow. Nucleation centres form so rapidly that the entire exposed layers of surface become completely covered.

The initial stage will be completed rapidly and the reaction will proceed through the transfer of a continuous layer into the interior of the crystal. The rate of propagation, which will depend on the nature of the diffusion layer and shape factor, will, after the rapid initial stage, be the *rate-determining factor*.

2. Where the rate of propagation is rapid and the nucleation rate is slow. In the limiting condition when one nucleation spot forms on the contact surface the reaction spreads from this centre and decomposes the entire particle. Thus, the rate at which nucleation occurs will be the *rate-determining factor* in such cases. Such a mechanism is to be expected in many solid-state reactions involving two

components. Nucleation can take place only at the points of contact between the two reactants, hence diffusion will proceed into the interior of each crystal from a relatively small number of surface points.

3. Where both nucleation and propagation rates are similar. A complex reaction curve may result which will be a function of the two individual rates. For a certain initial period of time, the rate may be mainly dependent on the number of nucleation spots and the rate at which each spreads. If the particles are of sufficient size, the second mechanism may predominate in the latter stages. The general form of such reaction curves is typically sigmoid-shaped.

EXAMPLES OF SOLID STATE REACTIONS IN CERAMIC MATERIALS

1. **Decomposition of Clay.** Murray and White¹ have studied the kinetical mechanism of the decomposition of clays and have concluded that, as the evolution of water is logarithmically related to time, the form is *first order*. Unfortunately, these authors were not able to assess accurately the loss in weight in the initial stages of the reaction because of experimental difficulties, hence the existence of an induction or nucleation period was not established. The authors suggest that propagation must be rapid relative to the nucleation rate as 'only then would a first order law be obeyed'. This is not necessarily correct for if the particles are assumed to be spherical, with the diffusion layer behaving purely as a linear agent of transfer (case *b*, p. 623), decomposition by propagation will be logarithmically related to time, as in equation (14b) irrespective of nucleation conditions.

Murray and White have deduced the energy of activation of various clays as follows:

Clay	Energy of Activation (cals/mole)
Supreme kaolin	37,970
Newton Abbot ball clay	34,310
Wyoming bentonite	57,640
Eureka halloysite	36,740

2. **The Quartz Transformation.** Grimshaw, Hargreaves and Roberts² have studied the kinetical mechanism of the destruction of quartz at high temperatures and have shown that two mechanisms can be ascribed depending on the presence, or otherwise, of catalytic agents.

(a) *Pure quartz.* When pure quartz, in the form of small particles, is heated to a sufficiently high temperature, a reaction takes place which results eventually in the total decomposition of the mineral. The reaction starts at centres on the surface of particles and these eventually merge together so that the reaction continues through the advance of an interface into the interior of each crystal. In large particles the reaction rate is complex whilst in fine-grained material (less than 60 microns) the decomposition proceeds at a logarithmical rate throughout.

¹ Murray, P. and White, J., *Trans. Brit. Ceram. Soc.*, **48**, 187, 1949.

² Grimshaw, R. W., Hargreaves, J. and Roberts, A. L., *Trans. Brit. Ceram. Soc.*, **55**, 36, 1956.

Careful experimental tests have revealed that both the nucleation rate and propagation rates are important but, whereas the former depends inversely on surface area ($1/r^2$) the latter is related to $1/r$ (p. 626). In coarse-grained material the propagation rate is more rapid and hence a slow initial induction or nucleation period is distinguished, whilst, in fine material, the two rates are comparable in velocity and the two regions are indistinguishable.

The diffusion layer formed in this transformation is of type *b* (p. 623) and it neither retards nor catalyses the reaction rate, which is to be expected in a polymorphic change.

The reaction rates in the nucleation and propagation periods have been deduced from the two equations:

$$\text{Nucleation} \qquad \ln \alpha = -kt \text{ (equation 15b)}$$

$$\text{Propagation} \qquad \ln \alpha = \frac{-3u}{r} t \text{ (equation 14b)}$$

and, by calculating the appropriate rate constants at several temperatures, the energy change in the two periods may be derived from the Arrhenius equation. This gave

Energy of nucleation: 124,000 cals. per mole.

Energy of activation: 96,000 cals. per mole.

(*b*) *Quartz and catalysts.* The transformation of quartz is greatly accelerated by the presence of certain oxides which have been termed catalysts. Many of these (including the alkali oxides and iron oxide), react by forming a liquid phase with silica and, in such cases, the reaction proceeds rapidly to completion. Other catalysts, of which the alkaline earth oxides are examples, react only in the solid phase. The kinetical mechanism of these latter catalysts was studied in detail. The relative effectiveness of the various agents was assessed by comparing mixtures containing an *equal number of similar-sized particles* of each oxide mixed with quartz grains; the number of contact points at which reaction must start was thereby kept constant in every case. The form of the reaction was similar in most cases. Initially, the rate of quartz transformation was very rapid but, after a brief period the velocity decreased rapidly and became comparable with the rate in the final stages of transformation in pure quartz.

The authors concluded that the particles of catalyst nucleate the quartz grains with which they are in contact and the transformation reaction is propagated very rapidly through those crystals. The catalytic effect is probably transmitted into a second ring of quartz grains which touch those in 'primary contact', but its influence is then dissipated and no further grains are attacked. Further reaction can then only proceed by the pure quartz grains reacting independently of catalytic activity of any kind.

This type of behaviour was found when calcium, magnesium and titanium oxide were added to quartz. Alumina was anomalous and appeared to retard the transformation at all stages; not only was there no initial period of pronounced catalytic activity, but the latter stages were also reduced in rate. Weyl has suggested that aluminium ions, being of high charge and small in size, more effectively screen

highly-polarised oxygen ions, and therefore inhibit the nucleation process. Furthermore aluminium more readily diffuses through a quartz lattice than other cations and can therefore affect more quartz particles.

3. Reactions between Mullite, Silica and Alumina and certain Carbonates.

Pole and Taylor¹ measured the reaction rates between these substances at several temperatures by calculating the amount of carbon dioxide evolved. The mechanism was shown to correspond to the case of a diffusion layer retarding the rate, as in equation (9) (p. 623). Sodium carbonate was the most effective reactant used and, in general, mullite was more readily attacked than quartz with corundum least of all.

4. **Reaction between Lime and Silica.** Jander and Hoffman² studied the reaction between lime and silica as a function of relative concentrations, time and thoroughness of mixing and found that the orthosilicate ($2\text{CaO} \cdot \text{SiO}_2$) was, apparently, the first product in all cases. When the proportion of lime was large, tricalcium silicate developed after long periods of firing, whilst the metasilicate $\text{CaO} \cdot \text{SiO}_2$ appeared in those mixtures with a lower concentration of lime. Water vapour was found to be an activator of the reaction.

HETEROGENEOUS REACTIONS

CLAY and many other ceramic materials are being used on an ever-increasing scale as catalytic agents to promote gaseous and liquid reactions. To quote an example, ethylene and bromine can be mixed together without reaction, although if they are contained in a glass vessel, reaction will proceed on the surface; however, if a small amount of clay is added, the velocity of the reaction is greatly accelerated.

Dupont and Dulou³ have described the polymerisation reactions of pinene at clay surfaces. Many condensation and alkylation reactions of the Friedel-Crafts type progress rapidly if a clay is used as a catalyst and Sachanen and Caesar⁴ have summarised many of the important applications in this field.

Reactions of this type are termed *heterogeneous* and always involve a surface which is capable of adsorbing the gaseous or liquid phase. The forms of such reactions are of interest and can be deduced as follows:

In a system composed of a surface and gas molecules, the latter strike the former, condense, remain on the surface for a time and then evaporate; eventually an equilibrium will be set up between the molecules impinging and those evaporating.

The number of molecules n which strike unit area of surface in unit time must be proportional to the pressure (p) of the gas and so, if a is the proportion adhering, an is the total number of molecules colliding with and being temporarily retained by a unit area in unit time.

Furthermore if S is the total proportion of surface covered at any instant then $1 - S$ is the amount of surface available for the condensation of more particles, hence, assuming monomolecular adsorption, the rate of condensation is $(1 - S) an$ moles. per sq. cm./sec.

¹ Pole, G. R. and Taylor, N. W., *Penn State Coll. M.I. Exp. Stat. Tech.*, Paper No. 20, 1935.

² Jander, W. and Hoffman, E., *Z. Anorg. Allgem. Chem.*, 218, 211, 1934.

³ Dupont, G. and Dulou, R., *Verre Silicates Ind.*, 12, 8, COBEA, 1947.

⁴ Sachanen, A. N. and Caesar, P. D., *Ind. Eng. Chem.*, 38, 43, 1946.

The rate of evaporation is proportional to the surface covered (i.e. S) therefore it can be expressed as VS where V is a constant.

At equilibrium, the rates of condensation and evaporation are equal, hence

$$(1 - S)an = VS \quad (16a)$$

or
$$S = \frac{an}{an + V} \quad (16b)$$

The adsorbed gas reacts on the receptive surface and, if the reaction velocity is small compared with the ratio of condensation and evaporation, the decomposition of some molecules will not appreciably alter the equilibrium condition.

The rate of reaction will be proportional to the concentration of molecules on the surface, raised to a certain power depending on the order of the reaction (see p. 614).

Hence
$$\frac{dx}{dt} = kS^m$$

where k is a constant depending on the rate of evaporation of product.

In unimolecular reactions $m = 1$ so

$$\frac{dx}{dt} = kS$$

Substituting in equation (16b):

$$\frac{dx}{dt} = \frac{k \cdot an}{an + V} = \frac{k \cdot \frac{an}{V}}{\frac{an}{V} + 1} \quad (17a)$$

Now n is proportional to the pressure of gas p and ka/V and a/V are constant under particular conditions, hence equation (17a) can be written as

$$\frac{dx}{dt} = \frac{K_1 p}{K_2 p + 1} \quad (17b)$$

So a reaction which involves a unimolecular change does not obey first order kinetics when it takes place where a surface layer serves as a catalyst.

There are two limiting cases:

1. When the surface is sparsely covered and molecules do not condense easily but evaporate readily. Then a is small, but V is high and S (the proportion of surface covered) is small. Therefore, $1 - S \approx 1$.

So equation (16a) becomes $an = VS$ and substituting the unimolecular form

$$\begin{aligned} \frac{dx}{dt} &= kS \quad \text{as above,} \\ \frac{dx}{dt} &= \frac{kan}{V} = Kp \end{aligned} \quad (18a)$$

i.e. rate is dependent on pressure so the reaction is truly unimolecular in such cases, but only when the surface adsorption approaches zero.

2. When the surface becomes almost entirely covered with adsorbed molecules $S \doteq 1$ so the rate equation is:

$$\frac{dx}{dt} = kS \doteq k \quad . \quad . \quad . \quad . \quad (18b)$$

The rate of reaction is independent of pressure and is of *zero order*. In other words the gas particles are retained immediately they collide with the surface and are not easily released. This is approximately the condition when organic molecules react at a clay surface.

There are thus two extreme cases of heterogeneous reactions given by the equations.

$$(18a) \dots \frac{dx}{dt} = kp \quad \text{and} \quad (18b) \dots \frac{dx}{dt} = k$$

Therefore the general case is

$$\frac{dx}{dt} = kp^x \quad . \quad . \quad . \quad . \quad (18c)$$

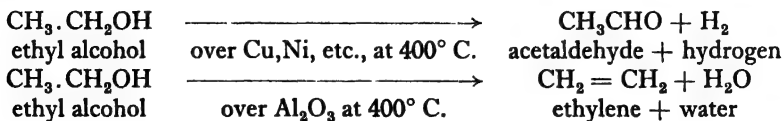
where x lies between 0 and 1. Hence such reactions have *fractional orders*.

The kinetical form of gas/surface reactions is complicated by the behaviour of the compound formed. In many cases, the product is strongly held by the surface and so retards the reaction, especially in the advanced stages, thus poisoning the catalyst.

When two reacting gases are involved, the rate of reaction depends on the relative adsorption capacity of the molecules of each type.

The mechanism of heterogeneous reactions or surface catalysis is not fully understood. Formerly, it was thought that, as the gaseous molecules are adsorbed on the surface, there is a localised concentration of reacting particles. It is now concluded that the surface layers hold the adsorbed molecules rigidly by virtue of the unsatisfied valency conditions in the outermost atomic groupings. The electron field of the gaseous molecule is, thereby, distorted and reactions can proceed which would, otherwise, be impossible.

This view is confirmed, to some extent, by reactions which lead to different end-products when different solids are used as catalytic surfaces. An example of this is the dissociation of ethyl alcohol vapour when passed over metallic surfaces such as copper and nickel, and over non-metallic materials like alumina. The change proceeds as follows:



The theory has been advanced that the catalytic surfaces attract different configurations or groupings of the alcohol molecule. The metallic surfaces containing atoms of a single type tend to attract hydrogen atoms only, whilst the alumina surface attracts alternate hydrogen and oxygen atoms as shown in Fig. X.63

Some surfaces contain active adsorption centres of more than one type. Thus platinum wire catalyses the decomposition of ammonia and also the dissociation of hydrogen iodide. If it is used for the former reaction it rapidly becomes 'poisoned' and inactive; but in this 'poisoned' state it will readily catalyse the latter change.

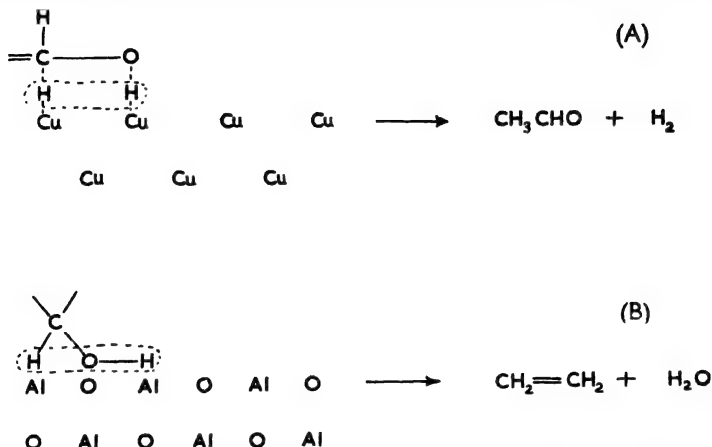


FIG. X.63. THE MECHANISM OF THE DISSOCIATION OF ETHYL ALCOHOL
At (a) a metallic surface; and (b) the surface of alumina powder

KINETICS OF ADSORPTION

HETEROGENEOUS reactions proceed by adsorption and as this phenomenon is a characteristic feature of clays, it is of special interest to ceramics.

The term *adsorption* implies a concentration of a particular component at the surface of another phase and, in theory, should be distinguished from *absorption* which implies internal penetration (see p. 419).

The amount of adsorption depends upon the surface area exposed, the concentration of so-called 'active centres' in the surface, the temperature, the concentration of adsorbent or the pressure, if a gaseous phase is involved.

The adsorption of gases or other molecules by a surface undoubtedly involves attractive forces, the nature of which can only be conjectured. Van de Waal forces (see Chapter II) have been suggested but, in recent years, a more tenable theory has been advanced by Fajans and developed by Weyl and others. Briefly, atoms and ions in the outermost surface layers are electrically unbalanced and the electron fields are distorted or 'unscreened'. Such units will readily link with molecules to reduce the unbalanced 'screening'. The rigid bonding between surface layers and adsorbed particles can only involve one molecular thickness because such forces act over a small distance. When deformation of the adsorbed molecule is high, however, extra layers may build up but they can do so only if the pressure or the concentration is high and even then they are much more loosely held than the first layer.

From a kinetical stand-point, adsorption can be treated in a similar fashion to heterogeneous catalysis. Equations 16a and b apply namely:

$$(1 - S)an = VS \quad \text{or} \quad S = \frac{an}{V + an}$$

where S is the proportion of surface covered and $a \cdot n$ is the total number of molecules colliding and adhering in unit time and V is a constant determined by the rate of evaporation. At equilibrium, the number of adhering particles per unit time will equal the number evaporating.

If the adsorbed layer is of mono-molecular thickness, the fraction of surface covered (S) will be proportional to the amount of gas (x) adsorbed by a mass of solid (m), and as n is proportional to the gas pressure p , the above equation may be written

$$\frac{x}{m} = \frac{k_1 k_2 p}{1 + k_1 p} \quad . \quad . \quad . \quad . \quad (19a)$$

where $k_1 = a/V$ and $x/m = k_2 S$.

This is known as the *Langmuir adsorption isotherm* and is frequently expressed as

$$\frac{p}{x/m} = \frac{1}{k_1 k_2} + \frac{p}{k_2} \quad . \quad . \quad . \quad . \quad (19b)$$

Hence a graph of $\frac{p}{x/m}$ against p will give a straight line and under standard conditions the surface area of powders can readily be compared (see Chapter VII).

There are two limiting cases:

1. When either the pressure or the degree of adsorption is low, only a small portion of the surface is covered hence $S \approx 0$ and $1 - S \approx 1$ and equation 16a becomes $an = VS$ which substituting as in equation (19a)

$$\frac{x}{m} = k_1 k_2 p \quad . \quad . \quad . \quad . \quad (19c)$$

i.e. the gas adsorbed is directly proportional to pressure.

2. When the adsorption is large $S \approx 1$ so equation (16a) becomes

$$(1 - S)an = V$$

$$S = 1 - \frac{V}{an}$$

$$\text{or} \quad \frac{x}{m} = k_2 - \frac{k_2}{k_1 p} \quad . \quad . \quad . \quad . \quad (19d)$$

As the pressure increases $k_2/k_1 p$ becomes smaller and x/m approaches the value k_2 . So at low pressures the adsorption is given by $x/m = kp$ and at high pressures by $x/m = k$.

At intermediate pressures or adsorptions the general equation $x/m = kp^n$ applies where n lies between 0 and 1.

Adsorptions from solutions by solid surfaces obey similar laws; the general equation is

$$\frac{x}{m} = kc^n$$

where c is the concentration.

The adsorption of dye-stuffs from solutions by clays is a typical example of this type of adsorption.

CRYSTAL GROWTH

IN the ceramic processes which have been considered so far, there has been a change in the physical or chemical nature of the original components. At high temperatures, however, many crystal forms increase markedly in size without any change in crystallographic type. In a similar way, compacted powders shrink when heated and form bonds which are purely the result of a change in crystal dimensions or of a development of a continuum between adjacent particles. The lattice arrangement in the parts of the crystal which form on heating is indistinguishable from that of the initial crystallites and, in addition, particles are linked together by the intermerging of their atomic or ionic configurations. Such crystal growth is termed *sintering* and is of especial interest in ceramic studies.

An important consideration in sintering processes is that the crystal growth takes place at temperatures well below the point of liquid formation.¹ For instance, periclase, MgO, does not fuse below a temperature of about 2,800° C. yet when fired in a rotary kiln at only 1650° C., minute crystallites will grow readily to an appreciable size. In a similar way mullite can be detected in kaolinite fired at around 1000° C. only by X-ray analysis. If the temperature is maintained at 1250° C., the crystals become large enough to be visible under a low-power microscope, yet the amount of the mineral present has not been substantially increased. The melting point of mullite (3Al₂O₃ · 2SiO₂) is 1810° C., so that a liquid phase cannot have been involved.

In recent years, considerable progress has been made in the manufacture of high-purity oxide refractories. Sintering plays an important role in their formation because a hard, dense body can be prepared by firing well below the liquidus temperature.

The fundamental mechanism of sintering is not yet fully understood, although many authorities consider that diffusion phenomena are involved. Crystal growth is undoubtedly intimately linked with the distorted surface layers of crystals and with the degree of compactness or number of contact surfaces within the mass. Three possible mechanisms have been advanced to account for the transfer of material (a) vaporisation and condensation, (b) plastic flow of material, and (c) solid diffusion.

Huttig² has demonstrated that significant changes can be detected in the cohesion and electrical conductivity of compacted metal powders at temperatures far below their melting point. This conclusion is supported by Clark, Cannon and

¹ The term sintering is frequently used in the ceramic industries to describe a certain condition in the firing of ware (see also p. 638). It represents a state of partial fusion when the mass has developed a degree of strength but is still porous. The individual particles have either grown, fused or been fused together but the bonding is confined to surfaces or points which are in contact. In the specialised usage of the term *sintered ware*, fusion is not implied because the crystal growth takes place at temperatures well below the lowest possible point of liquid formation.

² Huttig, G. F., *Z. Anorg. Chem.*, **247**, 221, 1941.

White¹ who have demonstrated that an alumina compact develops strength at about 600° C. This, they attribute to the removal of a hydrate layer and the formation of weak surface linkages which increase the 'screening' of the exposed oxygen atoms.

True sintering, however, which is manifested by the growth of crystallites and an increase in density of the compact, is usually acknowledged to start at the Tamman temperature which is about 0.55 to 0.60 that of the melting point of the component.

When sintering occurs, the mass of small crystallites changes slowly into a compact of a few large intergrown crystals. Microscopic observation suggests that each initial particle merges with its neighbours and the spaces between the particles progressively decrease and finally disappear, until eventually large, perfectly-developed crystals are formed.

There are two phenomena which are not easy to explain when crystals grow in sintered material.

1. Despite an initial random distribution, the small crystallites grow into well-developed crystals which are optically oriented throughout.

2. The void space between the sintering crystallites vanishes entirely without apparent diffusion of a gaseous phase.

Theories of the Mechanism of Sintering.

1. *Vapour phase transference.* Until a few years ago the most commonly accepted explanation of sintering was that of the transference of mass through the vapour phase. The vapour pressure of solid ceramic materials is known to be low at normal temperatures, but it is appreciable, and, as the temperature is raised, the pressure is substantially increased.

Any small particles with a large surface area will form a vapour phase more readily than large ones. Hence, material will be lost from smaller particles and will condense on larger grains. A compact of small particles will thus tend to change into a mass of larger grains and eventually into a single crystal. On this basis the formation of large uniform crystals is readily explained because the condensing phase would take up the lattice configuration of the 'accepting' crystal.

This theory receives little support at the present time because microscopic examination does not indicate that small particles decrease in size at the expense of larger ones, but that adjacent grains grow together and so form enlarged crystals.

2. *Diffusion mechanism.* A mechanism similar to that of diffusion has been suggested to explain sintering or crystal growth. Diffusion of ions from one lattice through a crystal of dissimilar type has been clearly established and it is to be expected that if vacant lattice sites or interstitial ions are suitably present, transfer between two similar crystal lattices is feasible. Undoubtedly transfer of ions in this way does occur in sintering processes, but it is unlikely that this is the principal mechanism involved. The calculated energy of activation required for self-diffusion reactions is much higher than the energy factor involved in sintering processes.

3. *Viscous and Plastic Flow.* Many authorities on sintering conclude that the transfer of material must be brought about by a shearing of layers by capillary forces between contact surfaces in the original compact.

¹ Clark, P. W., Cannon, J. H. and White, J., *Trans. Brit. Ceram. Soc.*, 52, 1, 1953.

The flow-process has been systematically investigated in the field of metallurgy¹ and it is concluded that the mechanism is mainly 'slip' within the lattice structure of the minerals. Crystals are known to be far from perfectly developed, and along certain planes of atomic configuration, dislocations may occur which, over a localised region, may destroy the symmetrical atomic arrangement. In such positions, the force required to move the atoms is far less than would be required over a normal part of the lattice and the weak forces which develop in the region of surfaces in contact may be sufficient to produce a movement, especially at high temperatures.

Clark and White² and Mackenzie and Shuttleworth³ have independently concluded that 'flow' must be the principal mechanism of sintering; the former as the result of experimental evidence from pure oxides; the latter from their work in metallurgical systems.

The equations which both groups of workers have derived are essentially similar and indicate that *plastic flow* with a definite yield point must be the main mechanism in the systems studied. This is in contrast to glass in which viscous flow (see Chapter XIII, p. 803) occurs. Clark and White suggest that in the initial stages of sintering, capillary forces in the region of contact surfaces produce flow in the material and thus build up a 'lens' between two adjacent particles.

Although the assumption of plastic flow, as the result of 'slipping' within the crystal lattice, offers a satisfactory explanation of the kinetical form of sintering reactions, there are many aspects which are still unexplained. Thus, certain materials are known to accelerate the sintering rate, but little is known of their operative mechanism. Many difficulties arise because a very small amount of a liquid phase will considerably increase the crystal growth and although most workers have used materials of high purity in their investigations, trace impurities, especially under the pressures developed by capillary forces could lead to liquid formation at temperatures well below the melting point of the mass. Even though amounts were small, traces of liquid would facilitate the transfer of material between crystallites.

FUSION AND CRYSTALLISATION

WHEN most ceramic materials are raised to a sufficiently high temperature they are gradually converted from a solid to a liquid material, often undergoing some decomposition in the process.⁴ According to the temperature attained the duration of the heating and some of the physical and chemical properties of such materials, the amount of fluid produced may be very slight and the term *incipient fusion* is then applied; a larger proportion of liquid may be produced and such a material on cooling is then said to be *sintered*, particularly if the liquid has been almost wholly superficial, i.e. when it forms a thin coating on many of the particles. When a large part (or the whole) of the material has been converted into a liquid the change is

¹ Mott, N. F. and Nabarro, F. R. N., Bristol Conf. on the Strength of Solids (*Phy. Soc., London*), 1948.

² Clark, P. W. and White, J., *Trans. Brit. Ceram. Soc.*, '49, 305, 1950.

³ Mackenzie, J. K. and Shuttleworth, R., *Proc. Physical Soc.*, B62, 833, 1949.

⁴ Some substances, which are so highly resistant to high temperatures that they undergo scarcely any noticeable change, are said to be *refractory* and to have the property of *refractoriness* (see p. 702). Hence, broadly, refractoriness is the converse of *fusibility*.

known as *fusion* or *melting*. *Vitrification* is an intermediate stage between sintering and complete fusion, but, it is becoming increasingly common in the ceramic industries to include all stages of partial melting as vitrification. The term sintering is seldom used except to describe the products from solid state reactions (see previous section) and occasionally in the production of frits and of some cements.

The complete change from the solid to the liquid state may be described as occurring in four stages:

Solid \rightarrow sintered \rightarrow vitrified \rightarrow fused or melted (liquid)

These stages tend to overlap because some fused material is produced in almost every stage after the heating has commenced and fusion occurs throughout the whole series of changes. These stages are, however, of great industrial and technical importance and should be clearly understood and appreciated.

Fusion is defined as the change in state of a substance from the solid to a liquid phase. It is usually brought about through the agency of heat, although pressure may also be an influencing factor. In ceramic and allied materials the term 'fusion' is preferred to 'melting' because, unlike many pure materials, the change of state takes place over a temperature range and a melting point cannot be established.

The change from a solid to liquid state can be explained on the basis of modern theories of the structure of materials. A solid crystalline material is composed of atoms or ions which are arranged spacially in characteristic groupings to give a symmetrical structure (see Chapter II). The distribution of electrical charge is such that each unit is maintained in an equilibrium position and although small vibrational movements may be possible they are insufficient to disturb the structure. As the temperature is increased, however, the atoms or ions are 'excited' by the heat energy supplied and the intensity of movement becomes greater. At some point the oscillation is sufficient to permit atoms to move out of their equilibrium position and hence the structure may break down completely. When this occurs the individual atoms or ions are virtually independent entities,¹ no bonds exist and the mass is capable of easy deformation. A liquid state has thus been formed.

THE MELTING POINT OF SIMPLE COMPOUNDS

ALTHOUGH the process of melting involves the separation of the cations and anions and the destruction of its structure, it is difficult to predict the temperature at which substances will melt except for the most simple compounds.

There have been many attempts to correlate the melting point of a crystal with a specific property such as the lattice energy, interatomic forces, type and character of the bonding, but none has been completely satisfactory and of general application. Weyl² has developed an 'atomistic approach to the melting of simple compounds' in which he suggests that as the temperature is increased, the defects in the structure increase and some cations occupy interstitial positions. Consequently some cations

¹ It is not strictly accurate to regard a liquid as being composed of individual units, because there is undoubtedly grouping of some type in most cases. However, if linkages do occur they are irregular and non-continuous and the structure is completely random.

² Weyl, W. A., *O.N.R. Tech. Report*, No. 52, 1952.

approach more closely to others and cation to cation repulsion forces are developed. Before a completely disordered structure can form, these repulsion forces have to be overcome and Weyl suggests that the melting point of a crystal is characterised by the thermal energy at which the cations can pass one another.

The theory advanced by Weyl satisfactorily accounts for the melting point of simple inorganic compounds and for a detailed explanation the reader is advised to consult the original publication.

Expressed simply, the following factors influence the cation to cation repulsion forces and hence the melting point of crystals.

1. The size and charge of the cation (see Chapter II). The smaller the size and the larger its valency the greater will be the repulsion between cations. This factor may be expressed as Z/r^2 where Z is the charge and r the radius of the cation.

2. The relative size of the anion. Large anions 'screen' small cations and so restrict their close approach. The repulsion forces which can develop are reduced and hence compounds with large anions tend to have a lower melting point than those of the same cation with smaller anions (Table X.VII).

TABLE X—VII. MELTING POINT OF ALKALI HALIDES

<i>Element</i>	<i>Fluoride</i> (1.36 Å)	<i>Chloride</i> (1.81 Å)	<i>Bromide</i> (1.95 Å)	<i>Iodide</i> (2.16 Å)
Lithium (0.60 Å)	842° C.	606° C.	549° C.	446° C.
Sodium (0.95 Å)	988	800	740	660
Potassium (1.33 Å)	846	768	728	693
Rubidium (1.48 Å)	775	713	681	642
Caesium (1.69 Å)	684	626	627	621

With the exception of the lithium compounds and sodium iodide, the melting points of the alkali halides decrease with increasing cation size and also with increasing anionic size.

3. The numerical ratio of anions to cations. When the number of cations in a crystal is small, the possibility of cations approaching each other is also small, and hence the melting point will be low. This is borne out by the following series:

Boron	Fluoride (BF ₃) . oxide (B ₂ O ₃) . nitride (BN) . carbide (B ₄ C ₃) decomp. at			
Melting point	—128° C.	450° C.	2000° C.	2350° C.
Anion to cation ratio	3:1	1.5:1	1:1	0.75:1

This same conclusion also applies to those compounds where the anion is of one type, but where the anion:cation ratio is increased by raising the charge on the cation. For example, in the following series of oxides, the cations are of comparable size but the melting point decreases as the anion:cation numerical ratio increases.

Oxide	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃
Melting point	2800° C.	2030° C.	1713° C.	570° C.	45° C.
Anion:cation ratio	1:1	1.5:1	2:1	2.5:1	3:1

There are, however, two opposing effects which give rise to apparent anomalies in the melting point of compounds. As the cationic size becomes smaller and its valency increases the repulsion force (Z/r^2) becomes greater, thereby tending to increase the melting point, but at the same time the anion:cation size and numerical ratio is also increased—a factor leading to a lowering of the melting point.

The influence of the two factors is well demonstrated in Table X.VIII where the melting points of some oxides are compared on the basis of the order of elements in the Periodic Table (p. 71).

TABLE X—VIII. THE MELTING POINT OF SOME OXIDES

	Group 1	Group 2	Group 3	Group 4
Period I	Li ₂ O > 1700° C.	BeO 2570° C.	B ₂ O ₃ 577° C.	CO ₂ gaseous
Period II	Na ₂ O 1275 (subl.)	MgO 2820	Al ₂ O ₃ 2050	SiO ₂ 1728
Period III	K ₂ O 430	CaO 2572	Sc ₂ O ₃ 2430	TiO ₂ 1850
Period IV	Rb ₂ O 400	SrO 2430	Y ₂ O ₃ 2410	ZrO ₂ 2720
Period V	Cs ₂ O 400	BaO 1923	La ₂ O ₃ 2315	HfO ₂ 2812

The ions of the alkali elements in Group 1 are comparatively large so the 'screening' effect of the anions is not very great. The principal effect is the repulsion term Z/r^2 and as this decreases with increasing size of the cation, the melting point decreases accordingly. The alkaline earth oxides of Group 2 with the exception of beryllia follow the same general pattern of decreasing melting point with increasing cationic size. Because the beryllium ion is small (0.31 Å) the repulsion term (Z/r^2) is large, but the possibility of the close approach of the cations is not great, due to the large anion:cation size ratio. The melting point of the oxide is, therefore, lower than magnesium oxide. For most of Group 3 and all of Group 4 the melting point increases with increasing size of the cation indicating a greater screening by the anions of the smaller cations, and this factor outweighs the repulsive force of the cations.

In the halide series of Table X.VII the anions are larger than oxygen and their greater screening effect (i.e. the influence of the anion to cation size) accounts for the apparently low melting points of all the lithium halides and sodium iodide.

With the exception of the alkalis the oxides of Periods 1, II, and III decrease in melting point with increasing cationic charge, showing the effect of increasing the numerical ratio of anions to cations. This trend is, however, reversed in Periods IV and V where with the increased relative cationic size, the repulsion term (Z/r^2) becomes dominant and so the melting point is increased.

This atomistic concept of melting is of value in explaining many anomalies in

the fusion of ceramic materials. If the atomic structure of a crystal is simple and all linkages and bonds between the component ions are identical, the energy required to cause breakdown will be similar at all parts and the material will have a definite melting point. In more complicated structures, involving several different kinds of atoms or ions and more than one type of linkage, some bonds will be broken at lower temperatures than others, and the fusion will occur gradually over a range of temperature even though the crystal is free from impurities.

Latent Heat. The process of melting involves an energy change which is virtually equivalent to the force required to break the bonds within the crystal. Consequently when liquid is formed, energy is absorbed from the surroundings and this is usually manifested as a heat effect. If a substance is steadily raised in temperature an 'arrest' invariably occurs in its heating curve and if the melting point is sharply defined, no further increase in temperature will occur until the substance has been entirely liquefied. The energy absorbed during melting or, conversely, that evolved during crystallisation, is termed the *latent heat*.

Most ceramic materials do not behave as simple compounds; on heating, the bond types are usually so varied that a long range of fusion occurs. In addition, the liquid formed is often so extremely viscous at temperatures near to the fusion point that complete disruption of the structure is not instantaneous. Furthermore, when the crystal lattice is mainly ionic, the energy required to separate the individual ions is invariably in excess of the bond strength itself and superheating effects are common. Similarly, on cooling, the crystallisation may be delayed or inhibited by a variety of causes which produce supercooling or 'retarded crystallisation'. For these reasons the temperature of fusion and the latent heat of ceramic materials are difficult to determine.

When another component is added to a substance the melting point of the latter is lowered unless a solid solution is formed (p. 549). This phenomenon is termed Raoult's law of the *depression of the freezing point* and the extent of the lowering (dt) is given by the formula

$$dt = \frac{RT^2M}{L}$$

where T is the absolute temperature; M is the molar concentration of the impurity; L is the latent heat of fusion; and R is a constant. This explains why eutectics, or points of lowest melting are formed between components.

Mixtures of components which behave in this way have a melting range on heating; at the eutectic temperature some liquid will form which will progressively increase in amount as the temperature is raised (see p. 545).

The Mechanism of Fusion in Ceramic Materials. There are three principal reasons why ceramic materials fuse over a range of temperature:

1. Several different minerals may be present in any one sample, each of which may have a different melting temperature.
2. Many bond types may occur in one particular crystal.
3. Eutectics may be formed.

Sharp melting points are known in ceramic mixtures but they are rare and can only occur in the following cases:

1. A pure component or congruently melting compound with only one type of linkage throughout its structure.
2. A mixture of the composition of a eutectic point.
3. Specific mixtures corresponding to a maximum or minimum in a solid solution diagram (see Fig. X.9, p. 553).

Even in these cases, melting will take place at one particular temperature only when the rate of heating is extremely slow, and when the quantity of material involved is very small in amount. When large quantities are heated, especially if the substance has a low thermal conductivity, or contains impurities, signs of fusion may appear at a temperature much below that at which liquefaction is complete.

The nature of the physico-chemical reactions which take place during the fusion of one or more ceramic materials can best be learned from a careful study of the appropriate equilibrium diagrams (p. 541 ff.), but it is important to realise that there is very little evidence as to the nature of the substances which are produced in the *earlier* stages of fusion, as most of the information which has been obtained relates to substances which have been either partially or completely fused and afterwards cooled prior to investigation.

The fusion point of ceramic substances is greatly complicated by the heterogeneous nature of these substances. Localised concentrations of individual components may give rise to partial fusion at temperatures well below those predicted by equilibrium studies. Conversely, a mass that is non-homogeneous may not liquefy until a temperature well above the theoretical fusion point because equilibrium is attained very slowly.

If the original substance is porous, a stage may be reached in which the pores are filled with liquid produced by partial fusion of the materials; this liquid solidifies on cooling, and the cold mass is then said to be *vitrified*. If the heating is continued to a suitable temperature, the whole of the material will become liquid and the mass is then said to be *completely fused*.

Rate of Fusion. It is impossible to devise simple formulae which will indicate the rate of fusion in terms of time and temperature because such fusion also depends very largely on the size of the grains of material in the surface exposed to heat or chemical action, and on the viscosity of the fused products; this viscosity depends on the nature of these products, some substances producing much more viscous fluids than others. Thus, magnesia produces a very viscous slag or glass and, consequently, the range of temperature through which fusion occurs (sometimes termed the *vitrification range*) is much longer where magnesia is the chief flux than when lime is present in considerable proportion. Thus, articles containing magnesia as a flux are less likely to soften and lose their shape than those in which lime is used.

The rate of fusion also depends on the solubility of the less fusible materials in the liquid portion. This, in turn, depends partly on their mutual reactivities—a fusible mobile silicate, rich in bases having a much greater solvent action than one—such as feldspar—of a more neutral character. The action of feldspar is very slow, so that it does not cause the ware to lose shape very quickly as is the case when calcium silicate is the chief constituent of the fused portion of the material.

The constitution of fused masses is by no means fully understood and there is much difference of opinion regarding the physical constitution of completely fused

salts. Some investigators maintain that such masses are composed of definite molecular compounds, whilst others regard them as dissociated into free oxides.

Modern thought inclines to the concept that there may be linkages between groups of atoms or ions in the liquid phase. Such units are not joined to others but behave as large isolated molecules. It has been suggested that groupings of this type have a marked influence on the viscosity of the molten mass.

The vaporisation point of a substance is that temperature at which it is converted into a vapour at normal atmospheric pressure. Many substances vaporise at temperatures well below their boiling point. Thus, iron oxide does so at about 1250° C. and more rapidly as the temperature is increased. Chromium oxide, copper oxide, barium oxide, and zinc oxide also vaporise freely at the temperatures reached in firing stoneware and porcelain. At the temperature of the electric arc most ceramic materials vaporise.

The rate at which vaporisation occurs depends partly on the temperature and partly on the vapour pressure (p. 528), each substance acting independently.

The boiling point of a substance is the temperature at which it is converted into vapour at such a rate that its vapour pressure is that of a column of mercury 760 mm. in length i.e. 1 atmosphere. Most ceramic materials have boiling points which are so high as to be outside the range of attainable temperatures, so that their boiling points are not of great importance. The chief exception to this is water, which, when pure, has a boiling point of 100° C. or 212° F. The boiling point of any substance is reduced if the pressure of the atmosphere in which it is heated is also reduced, so that water can be boiled rapidly *in vacuo* at about 60° C. and slowly at lower temperatures.

If a liquid is heated above its boiling point in a closed vessel so that the vapour of the liquid cannot escape, the vapour pressure will increase in proportion to the heat absorbed. A typical example of this is the pressure of steam in an ordinary boiler. Water heated under pressure has more solvent action than that at the ordinary boiling point, and this is probably one cause of the decomposition of felspar and other minerals from which clay is derived. Any substances which dissolve in a liquid will increase the boiling point of the latter in proportion to the concentration of the solution.

THE SOLIDIFICATION OF MOLTEN MASSES

WHEN a molten mass cools, it eventually becomes solid, but the physical and chemical nature of the product may vary greatly, according to the nature of the materials present and the rate of cooling.

The liquid state is a collection of atoms, ions or isolated groups of these with so great a vibrational energy that continuous linkages cannot form; hence *flow* can readily take place. As the temperature is decreased the movement within the liquid is reduced, more linkages can be formed and the mass becomes more viscous.

The atoms or ions in the liquid endeavour to combine with other units to preserve an electron balance, and at the same time, to form the most stable co-ordination (see Chapter II). The change from the virtually random arrangement of the liquid state to the symmetrical lattice of the crystalline medium, may involve considerable

displacement. In most cases, the liquid phase is sufficiently fluid to permit the complete crystallisation at a definite temperature, but, particularly in silicate systems, crystallisation is sluggish, because of increasing viscosity, and the liquid may 'freeze' with an unsymmetrical structure and form a *supercooled liquid* which is known as *glass*; the structure of such material has been described in Chapter III.

Crystallisation is a nucleation reaction (p. 626). At particular points in the cooling liquid, centres of incipient crystallisation begin to develop at the melting temperature and from them solidification progresses throughout the entire mass.

The number of nuclei which form determines the crystallinity of the solid. If many centres are nucleated at about the same time, the resulting solid is likely to be a mass of small crystallites; but if the number of nuclei can be kept to a minimum, only large crystals will be produced.

Nucleation depends, to some extent, on the rate of cooling; if this is rapid, many more centres are likely to develop before crystallisation is complete, than if the temperature had been slowly reduced.

In many cases, the formation of nucleation-centres does not readily occur and the liquid may supercool. If this is undesirable, crystallisation may be induced by 'seeding' the liquid with solid particles which provide centres for solidification.

Therefore, depending upon the composition of the melt and the conditions under which it is cooled, the solid formed may be (a) a homogeneous non-crystalline glass, (b) a wholly crystalline mass of either large or small particles, or (c) a heterogeneous mixture of both crystals and glass. If the cooling is sufficiently slow, all liquids will crystallise but, in some cases, the process is so slow that it cannot be completed in a finite time.

Quite often a glassy phase can be *devitrified* (i.e. caused to crystallise) by maintaining the solid at a high temperature, yet below the melting point. Thus, vitreous or fused silica is a true glass, but if it is held at a temperature in excess of 1200° C. it slowly crystallises to either tridymite or cristobalite.

When, on cooling, the components of a liquid can form solid solutions, the composition of the crystals depends on the rate of cooling (see p. 552). Thus, slow cooling will more nearly simulate equilibrium conditions and the solid phase will be homogeneous throughout; rapid cooling and crystallisation results in 'zoned crystals' where the internal composition is different from the external layers.

Crystallisation is accompanied by the liberation of heat which is equivalent to the *latent heat of fusion* absorbed in the melting process. The energy change is the difference in 'entropy' between the random state of the liquid and the ordered crystalline lattice of the solid.

If a liquid is slowly cooled and crystallisation is instantaneous at one temperature an 'arrest point' will occur on the cooling curve. The temperature will not fall further until crystallisation is complete. Should a glassy non-crystalline phase form, however, no 'kink' is noticeable and the cooling curve is perfectly regular.

THERMAL EFFECTS ACCOMPANYING REACTIONS

AS stated in the earlier part of this Chapter, reactions are accompanied by an energy change which is usually manifested as a heat effect. Thus a heat change may occur

when substances form, dissolve, combine, dissociate, melt or crystallise. The amount of energy involved in such changes depends on the initial and final states of the material. If the final state has a lower energy content than the original, heat will be evolved and the reaction is termed *exothermic*; conversely, if the final state has a higher energy content, energy will be absorbed and the change is *endothermic*.

HEATS OF REACTION AND FORMATION

If sufficient energy in the form of heat is available to cause the vibrational amplitude of a bond in a crystal to be exceeded, disruption of the lattice will occur, one or more new compounds may be formed, and the energy change is known as the *heat of reaction*; on the other hand, the material may melt with an energy change known as the *latent heat of fusion*; should the material be completely dispersed into individual atoms or ions then the accompanying energy effect is termed the *heat (or energy) of dissociation*, which is equal to but of opposite value to the *heat of formation*.

The heat of reaction is usually further subdivided and is known by the type of reaction which occurs. Thus, when minerals hydrate, the energy liberated is known as the *heat of hydration*; when they crystallise it is known as the *heat of crystallisation*; the *heat of solution* is the energy change when substances dissolve in a liquid medium; the *heat of combination* refers to the specific case when two or more materials react to form another.

The energy change on reaction is equivalent to the difference in lattice energies between the initial and final states. It is not easy to calculate on this basis alone although it can often be derived if the heats of formation of the components are known.

The heat of formation is defined as the energy change accompanying the formation of a compound from its individual constituent atoms. Thus, when water (H_2O) forms from two atoms of hydrogen and one of oxygen, a heat change of 57,826 calories per gram molecule is involved. The heats of formation of various other compounds from their elements and of various silicates are shown in Table X.IX.

TABLE X—IX. HEATS OF FORMATION OF SOME SIMPLE SUBSTANCES

Compounds	Calories per gm. mol.	Compounds	Calories per gm. mol.
H_2O	57,826	Na_2O	99,160
CO	29,290	K_2O	86,260
CO_2	97,616	FeO	64,040
SiO_2	198,300	Fe_2O_3	190,700
MgO	145,760	Fe_3O_4	266,910
BaO	133,100	$CaCO_3$	287,930
CaO	151,710	$MgCO_3$	267,390
Al_2O_3	389,490	$CaSO_4$	335,720
B_2O_3	279,810	$MgSO_4$	301,080

According to Hess's law, the quantity of heat evolved or absorbed by a reaction which takes place in two or more stages, is the same as would have been evolved or

absorbed if the reaction had occurred in one stage. Thus, the formation of carbon monoxide from carbon and oxygen is accompanied by the evolution of 29,290 calories, the formation of carbon dioxide from carbon monoxide by the evolution of 68,326 calories; in the formation of carbon dioxide from carbon, the same amount of heat (viz. 97,616 calories) is evolved as if the formation had taken place in the two stages just mentioned. Hence:

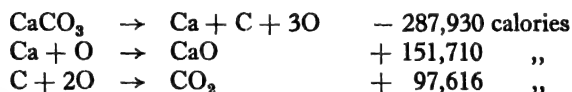
1. The heat of formation of a compound is independent of its mode of formation.
2. The thermal value of a reaction is independent of the time occupied by the process.
3. The thermal value of a reaction is the sum of the heats of formation of the final products of the reaction less the heats of formation of the initial products of the reaction.

According to Berthelot's law, 'every reaction which takes place independently of the addition of energy from outside the system, tends to form the combination which is accompanied by the greatest evolution of heat'. Hence, when carbon burns, CO_2 is formed in preference to CO . The final product, in any reaction, may usually be predicted by means of this law.

The amount of heat rendered latent when a compound is dissociated is often termed its *heat-content*. When heat is required to effect such a dissociation it is represented by a figure (preceded by a minus sign) after the equation describing the reaction. Similarly, when heat is evolved in a reaction, it is represented by a figure preceded by a plus sign.

The heat of reaction may sometimes be calculated from the heats of formation of the components and the products.

As an example the decomposition of calcium carbonate may be cited:

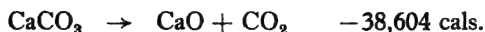


Therefore the total reaction which may be conceived as involving (a) a complete breakdown of CaCO_3 , and (b) the re-formation of CaO and CO_2 , has an overall energy change of:

$$-287,930 + (151,710 + 97,616) \text{ calories}$$

i.e. $-38,604$ calories per gm. molecule.

The difference between the initial and final states is thus 38,604 calories per gram molecule and the reaction may be fully represented as:



The equation indicates that, in the decomposition of calcium carbonate, heat is absorbed and the reaction is thus endothermic. When calcium is oxidised to form lime or when carbon is burnt and forms carbon dioxide, heat is evolved and the reaction is exothermic.

The latent heat of fusion is the amount of heat required to convert a unit weight of

solid wholly into a liquid at the same temperature. Thus, the latent heat of fusion of amorphous silica calculated by Richards and Vogt is about 65 calories per gram.

E. W. Washburn¹ calculated the latent heat of fusion of cristobalite from the formula:

$$L = \frac{RT^2x}{\Delta t}$$

where L is the molar heat of fusion, R is the gas constant, T the absolute melting point of the substance, Δt the lowering of the freezing point in some solution, such as the eutectic between cristobalite and alumina ($= 160^\circ \text{C.}$) and x the mole-fraction of cristobalite in the solution which is 0.0882. From these figures, Washburn estimated that the latent heat of cristobalite is 6,800 calories per mole, or 110 calories per gram.

E. W. Washburn² suggested the use of the following formulae, in accordance with the freezing-point solubility law, for determining the latent heats of fusion of refractory materials which form eutectics with each other. This law expresses the relation between the composition of a solution and the temperature at which it will be in equilibrium with pure crystals of either of its constituents.

$$\text{Log}_{10} x_a = \frac{0.219L_a(T_a - T)}{T_a T}$$

$$\text{Log}_{10} x_b = \frac{0.219L_b(T_b - T)}{T_b T}$$

where x_a and x_b represent respectively the molecular fractions of the substances A and B in the solution, L_a and L_b represent respectively the latent heats of fusion of one gram-molecular weight (or mole) of the substances A and B, whilst T_a and T_b represent respectively the melting points of the two pure materials on the absolute scale, and T is the eutectic temperature also on the absolute scale. This method may, however, be inaccurate on account of the possible presence of some unknown factor at high temperatures which brings error into the results. He gives the following figures for the latent heat of fusion of lime and magnesia:

TABLE X—X. LATENT HEAT OF FUSION

Substance	Fusion-point (Kanolt), °C.	Latent Heat of Fusion (cals. per gram)	Latent Heat of Fusion (cals. per mol.)
Lime	2570 ± 3	490 ± 20 per cent	30,000
Magnesia	2800 ± 3	700 ± 15 per cent	30,000

The latent heat of fusion of some complex materials is very high, possibly on account of their decomposition at the fusion-point; in that case, the heats of decomposition would be included in the latent heat of fusion.

¹ Washburn, E. W., *J. Amer. Ceram. Soc.*, 2, 1006, 1919.

² Washburn, E. W., *Trans. Amer. Ceram. Soc.*, 19, 195, 1917.

Table X.XI shows the heats of fusion of various complex materials.

TABLE X—XI. HEATS OF FUSION OF COMPLEX MATERIALS
(CALCULATED FROM THE HEATING AND COOLING CURVES)

<i>Substance</i>	<i>Melting-point °C.</i>	<i>Latent Heat (Cals. per gm.)</i>	<i>Heat of Fusion (Cals. per mol.)</i>	<i>Observer</i>
Anorthite	1532	100	28,000	Vogt
Diopside	1225	100	22,000	Vogt and White
Enstatite	1375	125	25,000	Vogt
Olivine	1400	130	18,000	Vogt
Akermanite	—	90	—	—
Calcium borate	—	49	—	—
Leucite	—	26	—	—

The latent heat of fusion is determined by the same physical factors which determine the melting point (p. 638). There is, therefore, a close relationship between these two values in many cases, but the parallelism is not entirely complete because the formation of complex groupings in the liquid may affect the determination of the absolute latent heat of fusion.

CHAPTER XI

CHEMICAL CHANGES IN CERAMIC MATERIALS

CERAMIC materials in an *unfired*, *unburned* or *green* condition are available in three states:

1. As raw materials—chiefly natural minerals, such as clays, sand, felspar, water, etc.
2. As prepared materials, such as those used as *bodies*, *engobes*, *frits* and for *glazes*, *colours*, etc.
3. As ceramic articles such as bricks, tiles, pottery, etc., prior to their being heated in an oven or kiln.

The chemical and physical changes which occur in such materials and articles are so numerous and varied that they are conveniently divided into two groups:

- (a) Those which occur at 'ordinary' temperatures—a term used rather loosely to include temperatures below 110° C.
- (b) Those which occur at higher temperatures, and particularly such as are reached in pottery ovens, kilns and furnaces.

Some physical and chemical reactions in and between ceramic materials start at or below ordinary atmospheric temperatures, but most of them then proceed so slowly that it is convenient to take a rather higher temperature (105°–110° C.) because this is the one used in chemical and physical laboratories for drying many materials and test-pieces. The reactions proceeding between 15° C. and 110° C. are almost wholly those which proceed at ordinary atmospheric temperatures though more rapidly at about 110° C.

Whilst there is no sharp dividing line between ordinary and high temperatures, the figure of 110° C. is particularly convenient in considering ceramic materials.

CHEMICAL CHANGES AT ORDINARY TEMPERATURES

THE *chemical reactions* to which ceramic materials are subjected at ordinary temperatures are chiefly due to: (a) water; (b) acids; and (c) alkalies.

Water has no rapid chemical effect upon most ceramic materials at ordinary temperatures, with the exception of certain metallic oxides such as lime, magnesia and calcined dolomite, which are hydrolysed more or less rapidly by it. Lime is the most rapidly attacked and magnesia least, dolomite being intermediate, as might be expected from its composition—the lime in the dolomite is most reactive.

Magnesia, when calcined at high temperatures, is converted into the stable oxide, periclase, and in this form, it is relatively unattacked by water. Lime, however, cannot be stabilised in this manner, but hydrolysis can be reduced by coating the particles with tar. Alternatively, the lime may be combined with silica to form

tricalcium silicate, which does not react with water. A process for the manufacture of small laboratory shapes of pure calcium oxide has been described by Williams.¹ Rehydration is reduced to a minimum by so preparing the raw material that the ware has an exceptionally low porosity. Some materials composed of calcium and magnesium silicates and aluminates develop hydraulic properties, and if present in burned dolomite may absorb water and cause disintegration of the calcined mass. Campbell² found that two calcium ferrates ($5\text{CaO} \cdot 3\text{Fe}_2\text{O}_3$ and $6\text{CaO} \cdot 3\text{Fe}_2\text{O}_3$) also develop hydraulic properties. The hydraulic properties of Portland and other cements are well known and are described in Chapter VI.

Caustic magnesia is very soluble in water and still more so in slightly acidified water, such as that containing carbonic acid, but magnesite bricks made of intensely calcined magnesia or periclase are practically insoluble in water or dilute acids, except on prolonged exposure. On the other hand, they are rapidly attacked by steam, so that they must not be brought into contact with humid gases or they will be disintegrated as the result of the expansion caused by the formation of hydroxides.

Most silicates, when subjected to the action of water for very long periods of time, tend to hydrolyse and although some change fairly rapidly, the reaction of others can be observed only in Nature.

Water has a pronounced influence on many other minerals some of which are common constituents of naturally-occurring clays. Probably the most important effect of water on clay is its ability to form ions from soluble components. The base or cationic exchange capacity (see p. 264) is of great importance in a clay, because it can greatly influence the texture. The type and concentration of absorbed cations is largely determined by the conditions during the deposition of the clay but they can be markedly altered if at some stage the clay has been subjected to leaching by percolating water, particularly if it is charged with cations of a different type. Calcium-bearing solutions have been known to assist in the consolidation of a shaley deposit, solely by a cationic exchange altering the colloidal properties of the clay.

The leaching power of water can also break down mineral components, e.g. feldspars, which 'weather' to form clay minerals under the influence of climatic conditions. Most alkali-bearing minerals are weakly ionised, and prolonged exposure to moisture is sufficient to cause a complete alteration of the mineral composition. It is likely that by a similar process some hydrous micas are produced by the leaching of primary micas which are richer in alkali.

Water is an intermediary through which other constituents may become active. Bacteria thrive in moisture and assist in the formation of carbonaceous components in soils and clays. Their action may, in turn, liberate acids which then attack other minerals which may be present.

The action of *carbonated water* (i.e. a solution of *carbon dioxide* in water) is, in some cases, relatively rapid, as is the action of rain water (containing carbon dioxide) upon limestone, basalts and olivines.

Water has a considerable influence on many other minerals, some of which are common impurities in natural clays. Thus, iron oxides may be converted into hydrates. Pyrite, FeS_2 , readily oxidises in the presence of moisture and forms

¹ Williams, A. E., *Trans. Brit. Ceram. Soc.*, 50, 215, 1951.

² Campbell, R. E., *J. Ind. Eng. Chem.*, 11, 116, 1919.

soluble sulphate. The physical effects of water in clays, after freezing, are described under 'Weathering' in Chapter VIII.

The direct reaction between water and fired ceramic ware is slow but nevertheless appreciable. Terra-cotta roofing tiles slowly rehydrate when exposed to atmospheric weathering and after several years service may have reabsorbed considerable moisture. Another serious complication attributable to water is that certain slightly soluble salts frequently present in fired clays may rehydrate and cause 'scumming' and 'efflorescence'. These faults are more commonly associated with the sulphates of calcium and magnesium and in addition to causing an unsightly brick, they often disrupt the shape as a result of the large hydration expansion.

The action of absorbed water in fired clay ware is frequently the cause of defects often attributable to other sources. Many of the faults which develop in glazed tiles and terra cotta, such as cracking or shelling of the glaze and some cases of delayed crazing, are due to the absorption of water by the body. If the absorption is of a chemical nature, the body itself expands, but more often defects arise either because of soluble salt action or due to the physical changes in water on freezing.

Delayed dunting (or cracking of a ceramic body either during storage or in use) is often due to the action of water which is absorbed by the body from humid air, even though the ware is stored under cover.

Acids may come into contact with ceramic materials in a variety of ways. Peaty or organic acids are frequently produced by bacterial action on carbonaceous constituents and can directly attack clays with which they are in contact. Rain water falling in an atmosphere rich in sulphurous and similar fumes may absorb sufficient gases to become distinctly acid. Many ceramic products are made specifically to withstand the attack of acids and are used as containers and transporters of such products in industrial practice.

Many acids will dissolve certain substances in clays and will alter their chemical composition as well as their physical form. Alkali-, alkaline earth-, and iron compounds are more readily attacked, although when in sufficient concentrations, strong acids decompose some of the clay minerals.

Hydrochloric acid attacks many calcareous and ferruginous substances, including dolomite, magnesite, calcite, iron oxides, etc., olivine, serpentine, chlorite, nepheline, epidote, leucite and apatite; some other phosphates, monazite, etc., are attacked to some extent. Some sulphides are also dissolved.

Calcined china clay and calcined halloysite differ from one another in that the latter can be completely dissolved in hydrochloric acid. Raw bauxite is readily attacked and completely dissolved by hydrochloric and sulphuric acids. When intensely calcined, however, it is practically insoluble. This is due to the crystallisation of the more stable forms of alumina, which begin to form at about 900° C.

Sulphuric acid when hot and concentrated attacks clays and other hydrated aluminosilicates and also most basic materials. When clay is heated for a long time with concentrated sulphuric acid the clay is decomposed, possibly with the separation of silica and the formation of aluminium sulphate.

Sulphuric acid also has the power of improving the working qualities of some shales. Only a very small proportion of acid is required—about 1 per cent of the

water used to soften the clay increases the modulus of rupture and the speed at which the clay-paste can be extruded through a die. No scum is formed as a result of adding the acid.

Nitric acid behaves in a similar manner to hydrochloric acid. In addition, it decomposes sulphides forming nitrates.

Phosphoric acid attacks silica glass and many silicates at temperatures above 400°C. , forming the corresponding phosphates and liberating silica. Calcined and crystalline silica is not attacked by phosphoric acid below 300°C. , but precipitated silica is attacked at lower temperatures.

Phosphoric acid also combines with silica to form a crystalline substance having the formula $\text{SiO}_2\text{P}_2\text{O}_5$, this substance occurring in four allotropic forms, two of the low-temperature forms being attacked by water rapidly, whilst the other two, which are stable at high temperatures, are insensitive to water or acids, even hydrofluoric. The resistance of siliceous glasses containing phosphoric acid to hydrofluoric acid is due to the formation of $\text{SiO}_2\text{P}_2\text{O}_5$, which is not affected by any acids.

Hydrofluoric acid decomposes many siliceous minerals which are unaffected by other acids, silicon fluoride being volatilised. Schwarz¹ found the following amounts of various kinds of silica to be dissolved by 1 per cent solution of hydrofluoric acid in one hour at 100°C. :

Quartz	5.2	} per cent
Tridymite	20.3	
Cristobalite	25.8	
Gelatinous silica	52.9	

These figures are not exactly comparative, however, because the solubility will be dependent on the surface area available for attack. In the examples considered, gelatinous silica is of fine particle-size whilst the quartz will be the most coarsely grained. When similar-sized particles of the three silica minerals are compared, quartz, the stable phase at room temperatures is slightly less soluble in hydrofluoric acid than the high temperature varieties.

According to Gautier and Clausmann, silica glass is only one-tenth as soluble in hydrofluoric acid as is ordinary glass.

Hydrofluoric acid or a similar derivative is occasionally employed to dissociate a complex silicate mixture and so facilitates its analysis. A few drops of concentrated sulphuric acid are added at the same time so that other radicals are converted to sulphates and the silica evaporates as silicon tetra-fluoride which is volatile and escapes to the atmosphere. This treatment should be used with care, as many minerals are not decomposed under these conditions and others only slightly so. Mullite and feldspars, both of common occurrence in clays and fired ceramic materials, are scarcely attacked by such reagents.

Sodium (and potassium) bisulphate when fused at temperatures of a dull red heat readily dissolve many silicates, but have no effect on quartz or the other allotropic forms of silica. This is the basis of the Trostel and Wynne² method for the chemical estimation of quartz in clays.

¹ *Z. Anorg. Chem.*, 76, 422, 1912.

² Trostel, L. J. and Wynne, D. J., *J. Amer. Ceram. Soc.*, 23, 18, 1940

Silica is very resistant to all acids, except hydrofluoric acid and phosphoric acid at high temperatures.

Silicon carbide is slightly attacked by hydrofluoric acid, but not to any great extent.

Acid-resistance. The most acid-resisting of ceramic materials are hard porcelains, some stoneware which closely resembles hard porcelain, and Staffordshire blue bricks.

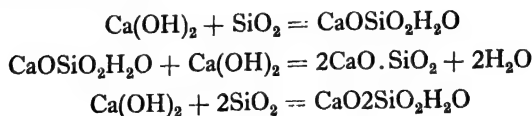
Where only a moderate resistance to acids suffices, glazed ware is usually satisfactory but to resist hot concentrated acids, the body of the ware should be fully vitrified and should contain a low proportion of alkali silicates. It should also have a minimum porosity.

Some bricks which appear to have been damaged by acid gases in the atmosphere—particularly from some factory chimneys—would have remained in satisfactory condition for many years longer if they had been fired at a slightly higher temperature or for a rather longer time near the conclusion of the firing.

Acid-resistant tiles are made from clays which can be well-vitrified at comparatively low firing temperatures. The degree of acid resistance is largely dependent on the porosity or water absorption of the body. Those with a water absorption of less than 1 per cent will not be attacked by most concentrated acids (except hydrofluoric or its derivatives) even at comparatively high temperatures. They are also little attacked by concentrated alkali solutions although some clays may be bleached by such reagents.

Alkalies usually combine with acid substances, but their action in the cold upon silicates and aluminosilicates is slight, and it is very feeble in the case of crystalline silicates. Freshly-precipitated hydrated silica is readily soluble in alkaline solutions. Flint is readily soluble in alkaline solution at 200° C., this fact being used in one method of making sodium silicate.

Some glasses and slags are readily attacked by hot solutions of alkalies, though some 'chemical glassware' and some glassware used for cooking utensils are highly resistant to such solutions. Silica reacts with some bases at a moderate temperature in the presence of steam. Use is made of this fact in the hardening of sand-lime bricks, the calcium silicate produced acting as a bond for the particles of sand. The following actions may occur:

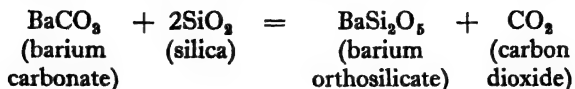


The briquetting of ores with lime, soda, and water-glass are similar instances of the action of alkalies upon silica in the presence of water.

Alkalies do not greatly affect silicates in the absence of water at temperatures below red heat or until the alkali salts themselves begin to melt. Reaction may then be quite rapid and most minerals are decomposed. Sodium carbonate is particularly reactive and is the material used for the fusion of silicates prior to a chemical analysis.

Barium carbonate combines with silica at temperatures far below the point of

liquid formation. In the pure form, barium carbonate will not dissociate below 1200° C., but in the presence of finely divided silica, carbon dioxide is rapidly lost below 800° C. The reaction may be expressed by the following equation:



The effect of reagents on most ceramic materials is not usually very distinct on account of the heterogeneous nature of the matter and the limited extent to which they may be attacked. Only in isolated instances can one mineral be separated from the rest, as before one is completely dissolved others will have begun to decompose.

REACTIONS AT HIGH TEMPERATURES

THE chemical changes which occur when unfired ceramic materials are heated depend on many factors; these include:

- (a) The mineralogical composition of the material.
- (b) The chemical composition.
- (c) The size-distribution of the minerals.
- (d) The areas of contact of the reacting particles.
- (e) The rate of heating at each stage or period.
- (f) The maximum temperature attained during the heating.
- (g) The duration of the heating at various stages or periods.
- (h) The atmosphere surrounding the material during the heating.

The chief chemical reactions which occur when ceramic materials are heated have been described in general terms in Chapter X. They may be grouped as follows:

1. Those which depend upon the effect of heat alone on a simple substance, and include: (a) dissociation; (b) rearrangement of atoms; and (c) decomposition.
2. Those which depend on the reaction of two or more constituents of a mixture, including substances present as impurities or purposely added, as in a fine earthenware body, or as a catalyst. These include: (a) displacement; (b) double decomposition; and (c) direct combination.
3. Those which depend on the presence of a gas (such as oxygen) in the atmosphere causing *oxidation*; or on carbon monoxide in the kiln gases which may cause *reduction*. The gas may be formed by the action of the air on one or more of the constituents of the ceramic material (as carbonaceous matter in clay) or on the fuel or it may be introduced directly in the gaseous form.

It is often difficult to decide which reactions occur and, in some cases, there is some doubt as to whether a change should be regarded as *physical* (e.g. the loss of moisture) or *chemical* (e.g. the loss of hydrate-water). R. E. Grim¹ includes the loss of all kinds of 'water' (whether 'free' or 'combined') on heating under the term *dehydration* but most ceramic chemists prefer to restrict dehydration to water lost at

¹ Grim, R. E., *Clay Mineralogy* (McGraw-Hill, London, 1953), p. 190.

temperatures below 110°C .¹ and all 'water' lost at higher temperatures as due to dissociation or decomposition, though there is some doubt as to how to describe the 'water' lost by some clays between 110° and about 640°C . There is probably no sharp distinction, though the assumption that the 'water' is lost at different distinct stages is convenient (see p. 417).

CHANGES IN COMPOSITION ON HEATING CLAYS

THE reactions which take place when clays are fired may be classified as follows:

1. Loss of hygroscopic and hydrate water.
2. Decomposition reactions:
 - (a) loss of combined water;
 - (b) decomposition of the oxy-salts;
 - (c) oxidation processes;
 - (d) reduction processes.
3. Re-forming reactions:
 - (a) recrystallisation.
 - (b) recombination.
4. Liquid formation.

The extent to which these reactions occur in any one clay depends on the nature of the minerals present and the temperature to which the sample is heated.

1. Loss of hygroscopic and hydrate water. The *loss of hygroscopic water* is usually complete at a temperature of about 100°C . The amount to be liberated depends largely on the fineness of grain-size of the minerals in the clay, because the moisture is associated with the surface area. Adsorbed water is not strongly held (see p. 420) but some clay minerals, particularly those of the montmorillonite type may absorb water between the plate-like layers of which the ultimate crystal is composed. Such absorbed moisture is more tightly retained and is not released until a higher temperature is reached. Most montmorillonites will lose their inter-layer water at about 150°C ., but the temperature depends on the type of absorbed cations which are present.

The amount of hygroscopic water retained by a clay is a function of the humidity of the atmosphere. Like all deliquescent substances, clays have a positive vapour pressure, hence the amount of moisture they can adsorb will be related to the partial pressure of water vapour in the surrounding atmosphere, or in other words, the relative humidity.

The amount of adsorbed moisture lost on heating to 200°C . by different types of clays which had previously been exposed to saturated air at 20°C . is given in Table XI.I.

¹ The loss of water at its boiling point under normal pressure (i.e. at 100°) is theoretically useful, but is seldom complete in reasonable periods of heating so that a rather higher temperature (105° – 110°C .) is generally used as the dividing line.

TABLE XI—I. HYGROSCOPIC WATER
CONTENT OF SOME CLAYS

<i>Type</i>	<i>Percentage weight lost</i>
Cornish china clay	1.2
Stourbridge fire clay	3.8
Brick clay	2.0
Ball clay (Dorset)	5.7
Bonding clay (Scottish)	7.4
Eureka halloysite	6.3
Wyoming bentonite (montmorillonite)	14.2

Water which is reversibly adsorbed may or may not be partially removed during the drying process. As outlined in Chapter IX, the principal aim in drying is to reduce the water used to facilitate moulding, to an amount below which no further shrinkage occurs. The amount of moisture still retained beyond this point may be considerable and it is not lost until the initial stages of firing in an oven or kiln. Articles made of clay are very friable when fully dry and it is, therefore, a technical advantage to place them in the kiln or oven whilst a small proportion of moisture is still present and the articles are in a black-hard rather than in a white-hard condition.

Only a small amount of water should be left in the ostensibly 'dry' articles or serious difficulties may arise. For instance, if the drying process has not been efficiently carried out and the evaporation of water is mainly from the surface, some migration of the colloidal mineral particles to the external faces of the ceramic shape may have occurred and this could lead to the formation of a 'skin' which restricts the easy removal of the last traces of moisture from the interior of the mass. If the temperature is raised too rapidly during the early part of the firing cycle, the entrapped water will volatilise and may crack or burst the body.

Hydrate water is defined as the water of crystallisation associated with salts and cations contained in the clay. The temperature at which it is removed is variable and there can be no sharp distinction between this form and the true combined water of typical clay minerals.

Two of the commonest examples of hydrates which occur in clays are the sulphates of calcium and magnesium. These minerals readily absorb water from their surroundings and form, respectively, gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and epsomite $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, but revert to the dehydrated form at temperatures in the region of 200°C . The absorption of hydrate water is usually accompanied by a volume expansion and the converse process, i.e. the removal of water, by a shrinkage. The amounts of hydrating minerals which are present in clays are insufficient to produce a noticeable effect but in the fired products, calcium and magnesium sulphates are frequently troublesome in producing efflorescence and also internal disruption due to the expansion caused by hydration.

In ceramic usage, the initial period of kiln firing up to about 150°C . is termed the *smoking period* (see p. 668).

2. Decomposition Reactions

(a) Many of the minerals associated with clays contain water as an inherent part of their structure. As the temperature is progressively raised such minerals decompose at specific temperatures with the evolution of water. Reactions of this type are not usually rapid and the loss of water frequently takes place over a range of temperature depending on the rate at which the temperature rises. Kaolinite, for example, begins to decompose at about 415° C., but at this temperature the reaction is so slow that it is partially complete only after several weeks of maintained heat; at 550° C., however, complete loss of water is effected in about 30 minutes.

The amount of water lost by each mineral depends on its crystal structure and the number of hydroxyl units contained in the lattice. The theoretical amounts held in some typical hydrous clay minerals are given in Table XI.II which also includes the temperature at which this water is given off at a rapid rate corresponding to the 'peak' in the differential thermal analysis curve for that mineral. This is not the initial temperature of decomposition, which may be 150° C. lower, but this point is difficult to establish with precision.

TABLE XI—II. THE DECOMPOSITION OF SOME CLAY MINERALS

<i>Mineral</i>	<i>Chemical Formula</i>	<i>Temperature of rapid decomposition</i>	<i>Percentage water lost</i>
Kaolinite	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$	585° C.	14.1
Halloysite	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$	558° C.	14.1
Montmorillonite	$\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$ (ideal)	678° C.	5.0
Muscovite mica	$\text{K}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ (ideal)	856° C.	4.5
Hydrous mica	As above but less alkali and more water	550° C. (upwards)	6.0–10.0
Gibbsite	$\text{Al}(\text{OH})_3$	325° C.	34.6
Goethite	$\text{FeO}(\text{OH})$	350° C.	10.1

Each of these minerals gives a pronounced endothermic heat effect on decomposition, so much so that they can be identified and frequently estimated by differential thermal methods (see Chapter V).

When such minerals decompose with the evolution of water, the solid products which remain are virtually an intimate mixture of the component oxides. The internal arrangement still has many of the characteristics of the original mineral and can be rehydrated to some extent, but, chemically, the oxide components have separate entities.

(b) Other minerals which are present in clays may also decompose when heated. These are limited almost entirely to the oxy-salts such as carbonates (CO_3) and sulphates (SO_4), which tend to lose carbon dioxide (CO_2) or sulphur trioxide (SO_3) at some stage of firing and are then converted to the simple oxides.

Calcium carbonate, calcite (CaCO_3) is the most common mineral of this type in clays and it is a frequent constituent of deposits of marine origin, where it is present as shells or the remains of sea-water organisms. It decomposes at a temperature of 880° C. with a weight loss of 44 per cent.

Magnesium carbonate, MgCO_3 , is associated with some clays although rarely in appreciable amounts, except in the form of the mineral dolomite $(\text{Ca,Mg})\text{CO}_3$. Carbon dioxide is evolved from magnesium carbonate at about 790°C . with a weight loss of 52.4 per cent. Dolomite, on heating, behaves as though it were a mixture of calcium and magnesium carbonates; under certain conditions, the loss of carbon dioxide takes place in two stages.

Sulphates of calcium and magnesium are not of common occurrence in clays although they may frequently form on firing by the direct combination of sulphurous gases in the kiln with other alkaline-earth bearing minerals. Both these sulphates dissociate to some extent at high temperatures (*circa* $1100\text{--}1300^\circ \text{C}$.) and may contribute to the *bloating* frequently associated with clays which vitrify at low temperatures.

The mineral *alunite* (see p. 321), has been reported in clays in Egypt and North America. It dissociates above 550°C . and liberates sulphur trioxide and water; the former is not entirely removed even after firing at a high temperature. Clay containing small amounts of alunite are used in the United States as a raw material for the manufacture of ladle bricks. Liberation of sulphur dioxide at the temperature of service, gives rise to a large 'after expansion' which seals the joints between adjacent bricks and prevents the penetration of molten metal into them.

(c) There are several mineral components which are of frequent occurrence in clays that readily oxidise at high temperatures.

Oxidation may be defined as causing oxygen (or its equivalent) to combine with a substance, forming compounds which, in the simplest cases, are known as oxides. More strictly, oxidation is a change whereby the proportion of the electro-negative constituents in a compound is increased as, for example, in the conversion of Cu_2O to CuO or of FeCl_2 to FeCl_3 . The conversions of -ous to -ic compounds are all examples of oxidation reactions.

Oxidation plays an important part in the various reactions involved in the production of ceramic articles. The chief technical objects of oxidation are:

(i) The conversion of impurities during the burning process (i.e. carbon, sulphur, etc.) into a form which can be easily removed, as by their conversion into gases or soluble substances.

(ii) The oxidation of iron compounds either to render them more refractory or for the production of a desirable colour, as in the manufacture of red bricks, terracotta, etc.

The removal of *carbonaceous matter* is most readily effected by oxidation, i.e. by heating it in a suitable atmosphere in which it combines with oxygen, forming carbon dioxide and water, both of which escape as gases. The temperature of reaction varies with the type of carbonaceous material (see Chapter VI). Algae and the carbonaceous matter in oil shales burn readily at temperatures around 200°C . When these are present, as they are to a considerable extent in clays of the Oxford and Kimmeridge beds, their oxidation reaction contributes to a more economical and uniform firing of the kilns. Ligneous or peaty components are oxidised at a higher temperature, but not as high as that required for bituminous or coaly material which does not burn readily until the kiln temperature has been raised to about 700°C .

Most fireclays contain a proportion of the last-mentioned type of carbonaceous material which, if it is present in appreciable quantities, is difficult to burn away. When anthracitic material is present in a clay, the oxidation reaction is extremely slow and such carbonaceous material is removed only slowly at temperatures of about $1000^{\circ}\text{C}.$, in an atmosphere rich in oxygen.

In many cases, it is of great technical importance that all the carbonaceous material should be oxidised in the early stages of burning, otherwise superficial fusion may occur, sealing the pores, thus preventing the access of air to the interior and so making it impossible to burn off all the carbon. If this should occur—as is liable in clays containing bituminous and anthracitic materials—a ‘black-heart’ may be formed which could cause disruption of the fired shape when in service. This may be avoided only by raising the temperature slowly—particularly between $350^{\circ}\text{C}.$ and $800^{\circ}\text{C}.$ and ensuring a free circulation of air.

Sulphides are decomposed when heated, if the atmosphere is oxidising, sulphates or sulphur dioxide and a sulphate being formed. Pyrite (FeS_2) loses 60–75 per cent of its sulphur at a temperature below $800^{\circ}\text{C}.$ and the remainder above this temperature. The latter is removed very slowly, the evolution decreasing in rapidity as the temperature rises; usually some combination occurs and a corresponding proportion of sulphur is never expelled.

Ferrous compounds are oxidised to the corresponding ferric compounds or to red ferric oxide when they are heated in a current of air. A temperature of $900^{\circ}\text{C}.$ is usually required for rapid oxidation, but if the temperature is very high the red ferric oxide (Fe_2O_3) may be decomposed and magnetic iron oxide (Fe_3O_4) produced.

Certain hydrates of iron which are of the ferrous form oxidise readily immediately the water is evolved. Siderite, FeCO_3 , is also oxidised on decomposition.

(*d*) *Reduction*, as a chemical term, may be defined as the removal of oxygen (or its equivalent¹) from a compound; it is, therefore, the converse of oxidation. More strictly, the reduction of a substance consists in an increase of the electro-positive charge or a decrease in its electro-negative charge.

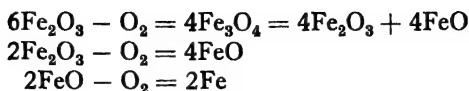
Reduction plays both a useful and a harmful part in the chemical reactions connected with ceramic processes. The chief reducing agents used in connection with ceramic materials are carbon monoxide and hydrogen (generally produced by burning coal with an insufficient amount of air), but finely divided carbon and several metals have a powerful reducing action when at a sufficiently high temperature. The presence of sulphur dioxide in the kiln gases, as occurs when a sulphurous coal is used, has a reducing effect upon any iron oxide present and may produce ferrous compounds. Sulphur trioxide, if present in the kiln gases, may attack the bases present in the clay and form sulphates. If an oxidising atmosphere is maintained these sulphates will persist and may produce a scum on the goods, but if reducing conditions arise they will be decomposed again.

Silica is reduced by carbon at temperatures above $1800^{\circ}\text{C}.$, forming the element silicon and carbon monoxide. The reaction is more rapid in the presence of iron and some other metallic substances. In some cases, silicon carbide or silicon monoxide

¹ The conversion of Fe_2Cl_6 to FeCl_2 is regarded as a reduction, though no oxygen is removed.

may be produced. Zirconia, when heated to very high temperatures, tends to be reduced by its combination with carbon, forming zirconium carbide.

The successive reduction of iron compounds may be represented by the following equations:



An instance of a *desirable* reducing action¹ is in the manufacture of blue bricks, where a vitrified mass of requisite strength is produced and also the blue colour which is characteristic of ferrous silicates. The slightly bluish sheen of porcelain is due to the same cause. Some colours used in glazes require to be fired in a reducing atmosphere in order to produce the desired effect.

Reduction processes are sometimes used in the manufacture of refractory materials, such as silicon carbide by the reduction of silica:



The reaction begins, according to Lampen, and also to Tucker, Gillet and Saunders, at a temperature of about 1820°–1920° C.; other carbides and carboxides are prepared in a similar manner.

A reducing action may be *harmful* when it is produced accidentally, as it may result in the decomposition of a useful material and the production of undesirable fusible compounds. Thus, if fully oxidised iron compounds, such as ferric oxide, are reduced to the ferrous state, in contact with clay or silica, they immediately lower the refractoriness of the bodies in which they occur, because ferrous silicate is readily fusible and may, therefore, cause much trouble and loss. Carbon has a stronger affinity for oxygen than iron, and, consequently, little or no oxidation of the iron compounds can occur in the presence of carbonaceous matter. It is, therefore, necessary to use a highly oxidising atmosphere in the earlier stages of firing clays, etc., containing carbonaceous matter, in order to oxidise and remove it. At a later stage, when all the carbonaceous matter has been burned away, some or all of the iron compounds may be reduced to the ferrous state without damaging the ware, but great care is needed in the control of the furnace or kiln, as in a reducing atmosphere at high temperatures the ferrous compounds will attack the silica present and form slag-like masses of fusible iron silicate.

Many of the 'black-cores' in fired clayware are due, not to undecomposed carbonaceous matter, but to iron in a reduced state. The latter can be recognised by a steely appearance and usually the dividing-line between the iron core and the clean body is sharply defined.

Carbon has a greater affinity for oxygen than sulphur; consequently, it may retard the oxidation of the latter, and, conversely, sulphates may, if required, be converted into sulphides by heating them in an atmosphere containing carbon monoxide or hydrogen at temperatures above 700° C. Reduction therefore forms a useful means of preventing the formation of 'scum' caused by soluble sulphates.

¹ Other instances of desirable reducing actions are the manufacture of *multicoloured bricks*, *black bricks*, and the *sang-de-bœuf* colour of some glazed ware.

Water at high temperatures has a very strong reducing action and also lowers the refractoriness of any fireclay or silica in contact with it, the refractoriness being lowered roughly in proportion to the amount of iron oxide present.¹

The reaction processes which take place in the initial stages of firing serve to decompose most minerals which are present and in effect reduce the clay to an intimate mixture of component oxides. In the latter stages of the burning cycle, crystalline compounds of an entirely new nature begin to form and spread throughout the mass.

3. Crystalline Formation at High Temperatures

(a) *Recrystallisation Reactions* are those in which the individual oxides undergo atomic transformations to form crystalline compounds.

Alumina, Al_2O_3 , is an excellent example; the amorphous form crystallises to the γ - (gamma) crystalline modification at a temperature between 500° – 1000° C. and at higher temperatures it is converted to the α - (alpha) form, known as corundum. In theory, the change appears relatively simple and to involve only the symmetrical arranging of the aluminium and oxygen atoms into configurations which are most stable under the specific conditions. However, the initial crystallisation to γ -alumina is complicated by the presence of impurities—particularly silica.

When *gibbsite* (trihydrate of alumina) or *diaspore* (monohydrate of alumina) is heated, water is evolved and at temperatures in excess of 550° C., both are entirely decomposed and only amorphous alumina remains. As the temperature is further raised γ -alumina begin to crystallise almost immediately although at a very slow rate.

Kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) also dissociates completely below 550° C. to an intimate association of amorphous alumina and silica, and remains in this form without recrystallisation until 980° C. when the alumina is instantaneously and completely converted to the γ -form.

Insley and Ewell² have shown that silica has its maximum inhibiting power on the recrystallisation of alumina when it is present with alumina in a molecular ratio of 2:1. The reasons for this unusual behaviour are not fully understood, but it is likely that the silica and alumina are linked by forces which, although weak, are sufficient to restrain the alumina from recrystallising. At higher temperatures, silica structures are readily broken down, thus freeing the alumina component (see also Chapter III).

Silica recrystallises from an amorphous form to either *cristobalite* or *tridymite* at a temperature of about 1250° C. This change is sufficiently rapid to be detectable by differential thermal methods, provided a sensitive recording equipment is employed. In most, if not every case, cristobalite is the first crystallisation product of amorphous silica at high temperatures. Tridymite may re-form rapidly from the cristobalite provided conditions are favourable, but there is no evidence to suggest that this phase may be the first crystallisation product.

Many natural forms of *amorphous silica* exhibit rapid crystallisation at about 1250° . This is particularly so of chalcedonic or flinty varieties and, for this reason, such materials are not suitable for the manufacture of silica bricks.

¹ Cf. Vickers, A. E. J., *Trans. Cer. Soc.*, 26, 177, 1926–7.

² Insley, H. and Ewell, R. H., *J. Res. Nat. Bur. Stand.*, 14, 615, 1935.

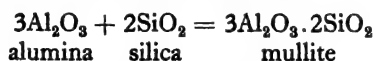
Crystalline *quartz* is one of the few minerals of common occurrence in clays, which does not break down to an amorphous form at some stage of the heating process. This mineral tends to convert to one of the other crystalline modifications of silica on prolonged firing, especially if suitable catalysts are present. The high alumina content of most clays, however, exerts a retarding action, so that fireclays, even after firing to 1250° and above, may still be rich in unchanged quartz.

Some other oxides may also crystallise at high temperatures although such changes are usually insignificant in clays. It is more than likely that such oxides would combine with other components or form a liquid phase at temperatures well below their crystallisation point. Thus, *magnesia* slowly transforms at high temperatures from an amorphous non-crystalline variety to the cubic form, periclase, but, when in contact with silica and the other component oxides of clays, it combines readily to form either stable silicates or, at higher temperatures, a liquid phase.

Anatase and, less commonly, *brookite*, are crystalline modifications of titania which are occasionally found in clays. These, like quartz, are not decomposed by heat although they are readily converted into the more stable variety, *rutile*, at temperatures as low as 400° C. In the presence of associated minerals, the transformation temperature may be appreciably altered.

(b) *Recombination reactions* are those which take place between two or more of the amorphous or crystallised components of heated clays. They are, in the main, processes which take place almost entirely in the solid state and so, like recrystallisation phenomena, are slow in reaching completion.

The best known example in clay systems is the combination of alumina with silica to form *mullite* in accordance with the equation



The temperature at which this reaction takes place depends upon many factors, such as the intimacy of the mixture and the presence of other components some of which accelerate and others which retard or even prevent the reaction. Mullite can be detected in some clays which have been heated to only 800° C., but the rate of reaction is not rapid below about 1000° C. Comeforo, Fischer and Bradley¹ have shown by electron microphotographs that mullite develops in pure kaolinite crystals at the approximate temperature of the exothermic thermal 'peak' at 980° C. When it is first formed, mullite is of extremely small crystallite size and cannot be resolved even under the highest magnifications of an optical microscope. On prolonged heating, especially at a high temperature, long needle-shaped crystals are formed which interlock and intergrow throughout the mass.

Mullite is a very stable phase in alumino-silicate mixtures of all types and is usually the first product to form in any mixtures where the two components are present.

Navias² has reported that the theoretical amounts of mullite were formed in all cases when a range of ball clays were fired to Cone 10. At higher temperatures

¹ Comeforo, J. E., Fischer, R. B. and Bradley, W. F., *J. Amer. Ceram. Soc.*, 31, 254, 1948.

² Navias, L., *J. Amer. Ceram. Soc.*, 8, 296, 1925.

side-reactions and liquid formation reduce the amount of mullite but it is always the principal crystalline component of fired aluminosilicates.

Many other crystalline products may be formed when clays are heated under favourable conditions, although in many cases they are a transient form which disappears into the glassy matrix on prolonged firing.

The reactions of *iron oxide* in a clay body are of especial interest because they are the main factors which contribute to the colour of the fired body. The most usual forms of iron compounds in clays dissociate at temperatures below 500° C. and if the atmosphere has been oxidising, ferric oxide only will remain. The colour of the mass at this stage will be red, but the tone and shade will depend on the amount of ferric oxide, its grain-size and the evenness of its distribution through the mass. At higher temperatures, reaction with silica occurs; if conditions are favourable, alumina may also be present in the crystalline phase and the mass then undergoes a pronounced change in colour. Definite crystalline modifications are difficult to identify because of the ease with which solid solutions are formed; furthermore, their existence is limited to a narrow range of temperature above which they melt to form liquid.

Clay minerals rich in iron oxide, such as the *nontronites* or *chlorite* types, form *fayalite* or iron-rich *olivines* (Fe_2SiO_4). *Pyroxenes* approximating to the composition $\text{FeO} \cdot \text{SiO}_2$ are also produced at temperatures around 900° C. possibly from the decomposition of less stable fayalite. Rigby¹ has reported that *iron cordierite*, ($2\text{FeO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$) occurs in the form of very fine crystals in the black cores of imperfectly-fired fireclay bricks.

Clays which contain nodular ironstone and carbonaceous material may form iron carbonyl if they are burned too rapidly or under non-oxidising conditions. The presence of this compound is a source of blowholes or 'blow-outs' in glazed ware which is bisque-fired prior to the glaze being applied; iron carbonyl gives off gas when in contact with water or when heated in an atmosphere of oxygen and there is frequently sufficient near to the surface to be glazed to cause serious defects.

Crystalline modifications of *calcium-bearing minerals* are also formed, especially in clays which are rich in limestone or chalk. *Calcium sulphate* frequently occurs on firing when calcium oxide is subjected to vapours or kiln gases rich in sulphur trioxide derived from sulphurous coal or other fuel, or from the decomposition of pyrites in the clay itself.

Silicates of calcium may, occasionally, be produced, although usually any free calcium oxide will combine with alumina and silica to form a liquid phase at temperatures below those at which crystalline modifications form rapidly. *α -dicalcium silicate*, $2\text{CaO} \cdot \text{SiO}_2$ is a constituent of Portland cement and is the result of firing clay with lime; it is also present in some fired brick clays of marine origin where the lime content is high. *Gehlenite*, $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, has been identified in engineering bricks although it may in such cases be a crystallisation product from a liquid phase rather than the result of a direct combination of the individual components. *Felspar*, corresponding closely to *anorthite* ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) is present in some

¹ Rigby, G. R., 'The Thin-Section Mineralogy of Ceramic Materials' (B.C.R.A., 1953).

fired clays, but more particularly when such products have been subjected to calcium-bearing slags at high temperatures.

Magnesium-rich clays occasionally form *forsterite* $2\text{MgO} \cdot \text{SiO}_2$ or *enstatite* $\text{MgO} \cdot \text{SiO}_2$ when heated around 1000°C . These minerals are not very stable in the presence of alumina and readily decompose or form a liquid. Grim and Bradley¹ have shown that magnesium-containing montmorillonites frequently exhibit a spinel phase (mainly $\text{MgO} \cdot \text{Al}_2\text{O}_3$) as a transient product when heated to about 850°C .

Alkali-bearing minerals are not common in fired clays, principally because both sodium and potassium oxides form liquids at temperatures well below those at which recombination reactions occur. After slow cooling or on prolonged exposure to a moderate temperature, alkali-containing minerals may crystallise from the glassy phase. *Leucite*, $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$, for example, may be present in fireclays used as blast furnace linings and *nepheline*, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, can be formed by the interaction of clays with soda vapour at high temperatures.

Crystallisation usually begins at small nuclei and hence the initial crystallites are extremely small. After long periods of firing at high temperatures these tend to grow or sinter unless otherwise destroyed by side-reactions (see also p. 683).

4. Liquid Formation. When a clay or other ceramic material is heated very slowly as under industrial conditions, the general order in which the changes leading to fusion occur is as follows: the smaller particles on the exterior of the mass tend to fuse first; they are followed by larger particles on the exterior. Later the particles nearer the interior behave in a similar manner. If the mass contains several substances or minerals, they will melt in order of their fusibility, though reactions which take place between some of them may alter this order considerably. This is particularly the case where a ceramic body or glaze contains a considerable proportion of fluxes, added so as to form a vitrifiable or glassy material in either small, medium, or large proportions according as the product is intended to be porous, vitrified, or completely fused. In any given mixture—provided the proportion of bases to silica is sufficient—the amount of fused material produced will depend on the temperature and duration of the heating; the higher the temperature or the longer the heating the greater will be the amount of fusion.

* In most ceramic materials, little glass is produced below a temperature of 1000°C . unless a considerable proportion of alkali is present. The glassy matter then usually begins to develop at about 750°C ., and increases fairly rapidly up to about 1150°C ., any felspar fusing readily about this temperature. The partial fusion continues rapidly up to about 1300°C ., the fused material dissolving the smaller particles and thus increasing the volume of the fused product. After this, the fusion proceeds more slowly, with a steady rise in temperature, because the aluminosilicates are more viscous and flow less readily than the simple silicates and so require a longer time to effect an equal amount of corrosion.

Liquid formation in clays commences at the temperature of the lowest eutectic point of the components in the mixture; then, with progressively increasing temperature, the amount of liquid phase increases rapidly. Alkali-bearing minerals or clays with a high content of adsorbed, exchangeable, alkali cations begin to fuse at low temperatures; a mixture of sodium, alumina and silica, for example, partially

¹ Grim, R. E. and Bradley, W. F., *J. Amer. Ceram. Soc.*, 23, 242, 1940.

melts at 732° C.; the equivalent mixture with potassium replacing sodium shows incipient fusion at 695° C.

Other cations also induce fusion in aluminosilicate mixtures at comparatively low temperatures. The eutectic temperatures for many of the common impurities in clay, when associated with alumina and silica are shown in Table XI.III.

TABLE XI—III. FUSION TEMPERATURES OF FLUXES IN ASSOCIATION WITH ALUMINA AND SILICA

Oxide	Lowest Eutectic Temperature °C.
Na ₂ O	732
K ₂ O	695
CaO	1170
MgO	1345
Fe ₂ O ₃	1073

Although some liquid usually forms in most mixtures at about the eutectic temperature, the increase in amount depends on many factors which include:

- (a) The temperature to which the mass is raised.
- (b) The amount of fluxing elements.
- (c) The grain sizes of the various minerals present and the evenness of distribution throughout the mass.
- (d) The rate of increase in temperature.
- (e) The time that the maximum temperature of heating is maintained.
- (f) The viscosity of the liquid formed.

(a) From phase equilibria studies the increase in the amount of liquid with the temperature of heating may be predicted. In some cases, small variations in temperature do not cause a pronounced change, but in other cases the quantity of liquid may substantially increase over a small temperature range (see also p. 570).

(b) The amount of fluxing elements present in a clay will influence the extent of liquid formation as will be evident from a study of the appropriate equilibrium diagrams (see Chapter X). There is, however, a further complication in that some liquids readily dissolve other components at temperatures well below those predicted by equilibrium studies. Free silica, for example, may be incorporated into a liquid phase in large amounts, especially if it is of fine grain-size and where alkali oxide are the fluxing oxides. Under favourable conditions, one molar percentage of alkali oxide may liquefy up to 20 molar parts of silica and even more may be incorporated if small amounts of alumina are also present.

(c) The grain size of the minerals containing the fluxing elements is important because it determines the distribution of the molten liquid throughout the clay mass. Alkali-bearing micaceous minerals are of frequent occurrence in clays and the particle size of this component largely determines the vitrification rate at a particular temperature. If the mica is of small grain-size the alkali ions contained in the lattice can react more readily with the clay and form the maximum of liquid in the shortest

fired clays, but more particularly when such products have been subjected to calcium-bearing slags at high temperatures.

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possible time. On the other hand, coarsely grained mica tends to form isolated regions of liquid around the edges of the grains but the spread of liquid throughout the body is not very rapid.

(d) The *rate at which the temperature rises* affects the amount of liquid formed because combination reactions are slow and require a considerable time to reach completion. A slow increase in temperature affords more time for the liquid phase to diffuse through the body and therefore to cause maximum reaction.

(e) *The time that the maximum temperature of heating is maintained* determines to a large extent, the uniformity of the product. If insufficient time is allowed at the maximum temperature, the amount of liquid which forms in the exterior of the article may be greater than that formed in the interior. It is advisable that ware should be held at top temperature for as long as is practicably possible, especially if large shapes are being fired.

(f) The *viscosity of the liquid phase* produced influences the total amount formed because a highly mobile liquid penetrates and interdisperses throughout a body more quickly than one which is viscous and flows slowly and irregularly. The more mobile liquid will come into contact with a greater proportion of soluble components than the more viscous one and will form a greater quantity of liquid in the same time interval.

The viscosity of a silicate melt is dependent on its composition and temperature. In general, the viscosity at a particular temperature, will decrease as the amount of fluxing elements increases. Alumina and, to a lesser extent, titania exerts an unusual influence on the liquid produced on heating silicates. Both aluminium and titanium cations can replace silicon as a network former in glass structures (see p. 175). In small amounts these may reduce the viscosity of the liquid phase of such glasses, but if larger amounts are incorporated the mobility is usually reduced because of 'induced' structural forms in the liquid phase. Magnesium oxide and silica form extremely viscous liquids, but when alumina is added to such mixtures, it increases the mobility.

The liquid state is always a temporary one, so far as ceramic materials are concerned. As soon as the liquid begins to cool its physical properties change, its viscosity increases and any chemical reactions are slowed down and eventually cease.

Many changes occur in the cooling stage—chiefly resulting in the formation of crystals and of glass or a mixture of these. Most of the crystals are much too small to be visible to the unaided eye and many ceramic materials therefore appear to be amorphous.

CHEMICAL REACTIONS IN KILNS AND OVENS

SOME of the most important chemical reactions between ceramic materials occur during the process of burning (or firing) the articles in an oven or kiln.¹

¹ In the ceramic industries the distinction between an oven and a kiln is that in a *kiln* the goods are heated in contact with the flames or hot gases from the fuel (though in some cases they may be protected by being placed in *saggars*) whereas in an *oven* or *muffle-kiln* the goods do not come in (obvious) contact with the hot gases. The distinction is often disregarded and tunnel kilns with cars are sometimes known as tunnel ovens and pottery kilns in which the goods are placed in *saggars* are often known as ovens.

Industrially, three different terms are applied to the heating of ceramic articles:

(i) *Baking* refers to heating to a moderate temperature, e.g. not exceeding a bright red heat. In many cases it may be said to correspond to the end of the decomposition stage (p. 657).

(ii) *Burning* refers to the heating, independently of the temperature or the duration. It differs from 'baking' in implying that a higher temperature has been reached and that further changes (in addition to decomposition) have occurred. The term 'burning' is also used to imply destruction of the material heated, as when fuel is burnt; to avoid misunderstanding many ceramists prefer to use the word 'firing' instead of 'burning' when heating the ware is implied.

(iii) *Firing* is a term which should be restricted to the placing of the fuel on the fire and all the actions necessary to keep it properly burning, but it is often applied to the whole process of heating the goods, as in the phrase 'the kiln is fired in order to bake or burn the goods'.

All these terms are used loosely, but the term 'firing' is gradually replacing the term 'burning'. A distinction should still be made between 'burned', meaning heated and 'burnt' meaning damaged or destroyed by heat; thus china-ware is burned, but fuel is burnt.

The industrial purpose to be served by the heating of clay and allied articles is the production of a mass or an article composed of 'solid' particles united by a glass. The solid portion may be crystalline or amorphous (or partly of both) according to the purpose for which the product is to be used; its crystalline nature is, for many purposes, of much less importance than that of the glass, for it is the latter which determines many of the essential properties of the product, though in some cases the crystalline portion is also essential. Until the great importance of the glassy material in ceramic articles is realised it is difficult to control their properties and behaviour.

In the finest products, such as the various porcelains and some stoneware, the significance of a crystalline fibrous or matted aggregate should also be realised; the nature of this is also dependent on that of the glass from which the crystals are largely produced.

In bricks, roofing tiles and some other building materials made of clay, the proportion of glass is relatively small, but its nature, distribution and amount are of great importance.

The chemical reactions which occur during the heating in ovens and kilns are usually described in five groups or stages:

Drying or *Smoking*, in which the articles are heated to a temperature not exceeding about 150° C.

Preheating, which includes some decomposition, the oxidation and the *water-smoking* of the goods, i.e. the period in which the clay is partially decomposed and its combined water liberated and passed out through the chimney.¹ The preheating stage of firing normally covers the temperature range 300–800° C.

¹ The steam or 'white smoke' which issues from the chimney at this stage of the firing is produced by the completion of the drying of the goods and by the water liberated on the decomposition of the clay.

The Full Fire Stage includes the cycle within the temperature range above 800° C. to the maximum temperature attained. In this stage, the kiln or oven is usually heated at its maximum rate.

The Finishing Stage or the *Soaking Period* represents the period during which the maximum temperature of heating is maintained. The principal recrystallisation, recombination and liquid formation reactions take place during this period.

The Cooling Stage is the period of time during which the burned articles are reduced in temperature from the maximum temperature of heating to a point at which it is safe and convenient to remove them from the kiln or oven.

The effects of heat in burning or firing ceramic articles are most conveniently studied by considering separately each stage in the process, commencing with the effect of a very gentle heat—technically termed ‘smoking’—and proceeding until the final or ‘finishing stage’ of the firing is reached. It must, of course, be understood that there is no sharp line of demarcation between these various stages, the effects of heat being continuous, so that the division of the firing into several ‘stages’ is wholly empirical.

Smoking. When a piece of clay or an article made of clay and allied materials which has been dried to the extent customary in manufacture is placed in a kiln or oven, the first effect of the heat is to remove any moisture still remaining in the material. It is by no means unusual for 5 per cent of water, equivalent to 1 cwt. or 3,000 cubic feet of steam per ton of goods, to be present in the ‘dried’ articles taken to the kiln and to be evolved as steam during the first stage of heating. For the steady evolution of this enormous volume of vapour without any damage to the contents of the kiln, it is very important to provide ample ventilation and to take precautions that the temperature shall not rise too rapidly, as, otherwise, the goods may be cracked by being unable to withstand the pressure of the steam produced in their interior and unable to escape with sufficient rapidity through the small pores in the articles.

The first or ‘smoking’ stage of the burning of ceramic materials is finished at a temperature of about 120° C. When this temperature is attained throughout the kiln and its contents, the whole of the water should have been vaporised and the second stage of heating may then be commenced.

At so low a temperature as 120° C. very few chemical changes occur, other than those produced when the heating is effected by waste gases bearing products of combustion from another part of the kiln. Such gases often contain sulphur trioxide which can combine with any lime present in the clay and, in the presence of moisture, may form calcium sulphate in the form of a white deposit or ‘scum’ on the surface of the goods.

The **decomposition stage** is the second stage in the burning or firing of ceramic materials; its range of temperature extends from about 300° C. to about 800° C., and in this interval many important chemical and physical actions occur (p. 657). It is usually essential at this stage that the temperature shall rise very steadily, though the rate of heating may vary within wide limits with different materials.

At a temperature between 300° and 800° C., many chemical changes commence which are not completed until a higher temperature is attained, but having once started they proceed gradually and are completed (as far as this is permitted) in the

next stage of the burning. Thus, the bases present as impurities in the material or produced by the action of heat on carbonates, etc., begin to attack the silica and alumina also present and, conversely, the acidic materials react with bases. By this means, fusible silicates and alumino-silicates are produced and if they are sufficiently numerous and have a sufficiently low melting point, an appreciable amount of glassy or vitreous matter will be formed to surround many of the individual particles and partially to fill the pores or interstices between them.

Apart from the reactions which result in the production of a fused glassy material, the chief changes which occur at this stage are oxidation processes which depend for their satisfactory completion on the presence of an ample supply of air. As these changes occur in the order of their affinity for oxygen, the heating must be properly controlled or undesirable reactions may occur whilst desirable ones remain incomplete. Thus, carbon has the greatest affinity for oxygen, so that in a highly porous and heat-resistant body the oxidation of compounds of iron, sulphur, etc., will not be completed until all the carbonaceous matter has been fully oxidised, and where the latter is present in large quantities it is important that the temperature should rise sufficiently slowly to remove the carbonaceous matter entirely before too high a temperature is reached. Otherwise, as the heat is nearly always applied externally to the materials,¹ the exterior may be raised to such a temperature that partial fusion occurs and the exterior pores are thereby sealed before all the carbonaceous gases can escape. The result of such sealing will be shown at a later stage by the articles being swollen or bloated by the pressure of gases in their interior. The appearance of the articles may also be spoiled by the charred material remaining behind and being incapable of oxidation because the air in the kiln cannot gain access to it on account of the sealed pores.

The nature of these oxidation processes have been discussed on p. 658.

The **full-fire stage** in burning ceramic ware commences at that temperature at which the kiln or oven may be heated as rapidly as is possible without serious risk of damage to its contents. In the case of some clays, it probably commences at about 800° C., but it is usually safer to regard it as commencing at 900° C. with some reservation with respect to the more fusible clays, glazes, etc.

The 'full-fire' stage is in every respect an intermediate one and in it the various chemical and physical changes which commenced in the prior, or decomposition stage continue at a more rapid rate, some of them reaching completion. In it, recombination reactions, partial fusion and some recrystallisation occurs and, if the temperature is sufficiently high or sufficiently prolonged, the molten liquid readily penetrates the pores in the more refractory material, dissolving some of the latter and so producing a still further quantity of the fused glass, slag or 'vitrified matter'.

The chemical changes which occur in this stage are not essentially different from those in the latter part of the previous stage. They consist chiefly in the combination of the bases or basic silicates with a further amount of silica. The higher the temperature attained in this stage, the more complete will be the chemical reactions between the basic and acid materials present and the greater the amount of silica

¹ The only exceptions being clamp bricks and some articles in which sawdust or other combustible matter forms an essential part of the material of which they are made.

entering into solution in the fused portion of the material. These reactions are more conveniently considered separately (see *Vitrification*, p. 672).

The **finishing stage** of the firing of ceramic ware is that in which the desired reactions and other changes are completed or have progressed to such an extent as to produce articles or materials having the requisite properties. In this stage the temperature of the kiln or oven does not rise appreciably above that of the full-fire stage. On the contrary, it should usually be maintained as constant as possible. For this reason, this period is often known as the *soaking stage*, the materials or articles being regarded as 'being soaked in the heat' until it has penetrated completely through them in much the same manner as water will penetrate a porous material immersed in it for some time.

The purpose of this prolonged heating or soaking at an almost constant temperature is to enable the various changes which have commenced in previous stages to be completed or at any rate to progress to an extent which will produce the desired properties in the product. If the temperature is allowed to rise rapidly until the firing is finished there is always a danger—except with the most refractory materials—that the articles will be distorted or their colour or other desirable properties will be spoiled by overheating. This serious defect is largely avoided by maintaining the temperature at an almost constant level during the last stage of firing, as this procedure enables the process to be more satisfactorily and readily controlled.

An adequate soaking period at 1100–1200° C. (i.e. prior to the final finishing at a higher temperature) is very important when firing china ware, porcelain and vitrified ware; it allows the necessary time for reactions to proceed as fully as may be required.

This prolonged heating or 'soaking' at a suitable high temperature may have the following effects:

(a) It may increase the amount of fused matter and, consequently, the amount of chemical action between the fluxes and the more refractory constituents, thus producing a larger amount of vitrified or glassy material which will gradually fill the interstices between the other particles, rendering the whole impermeable, as in the case of stoneware, or even translucent, as in porcelain.

By allowing ample time for the various chemical reactions to occur, prolonged heating of a ceramic material at the close of the firing imparts great stability to the material as a whole and enables a state of stable equilibrium to be attained. This is very important, when the product is to be reheated in use, as an unstable product—due to insufficient 'soaking'—will continue to undergo various physical and chemical changes which may have very serious consequences. The heating must not, of course, be prolonged to such an extent that undue distortion or loss of shape (see *Squatting*, p. 745) occurs. It is in the avoidance of this defect that the skill of the fireman is revealed, for the chemical reactions which are facilitated by the burning process must be stopped before they have proceeded too far. In other words, in the production of ceramic ware, most of the chemical reactions possible between the various constituents can never be completed, as that would render the material quite useless for the purpose for which it is intended. In this sense, as J. W. Mellor has pointed out, the chemistry of the firing of ceramic substances is a chemistry of arrested reactions. Unless the arrest takes place within a very narrow range of time or temperature, the product will be spoiled, hence, the enormous importance of

as complete a control as possible over the kilns or ovens in which the burning is effected.¹

The extent to which the burning of ware in a kiln has been completed is still often judged by observing the squatting of cones of known refractoriness value, set in a convenient position in the kiln. Although such methods are undoubtedly of value, they can be misleading if their full significance is not appreciated.

A cone squats because it has become sufficiently vitrified to flow under its own weight; it will be influenced not only by the temperature of its surroundings but also by the rate at which the temperature has been increased. The point at which a particular cone bends depends upon the amount of *heat work* it has received which is an integration of temperature and time. Seger Cone 7, for example, bends when the surrounding temperature is 1230° C. provided that the rate of rise of temperature has been 10° C. per minute; when the temperature is raised at 1° C. per minute cone 7 will bend at 1140° C., and at still lower temperatures under slower rates of temperature increase.

Each standard cone has a different chemical composition and when they are used as temperature indicators in kiln firing, each may have different vitrifying characteristics. It is not unusual to see during the latter stages of slow firing in a kiln that a cone of higher value will bend before one of nominally lower value; this is more likely to be due to anomalous softening behaviour—the cone of higher value having a greater softening range—than to deficiencies in the composition of cones—which are checked under a standard heating rate of 10° C. per minute.

The vitrification behaviour of ware being fired alongside standard cones may be such that two separate kiln firings, each to the same nominal cone value, may produce a very different degree of burning in the ware. This is because the rate of heating had been different in both cases.

The only correct way to ensure reproducible firing conditions in intermittent or continuous chamber kilns, especially when firing clay ware, is to use a reliable temperature recorder measuring at several points in the kiln. A heating rate must be predetermined and in every firing, the same cycle must be followed closely.

In most of the chemical processes employed in other industries the principal object is to complete the reaction as rapidly as possible consistent with obtaining the maximum yield of the desired product. This is not the case in firing ceramic wares, as the possible reactions cannot be allowed to proceed to completion, but must be stopped at a point which enables the product to possess the complex series of properties which are essential to its use to the best advantage. Anyone with even a small knowledge of chemical reactions knows how difficult many of them are to arrest even when they take place at the temperature of boiling water, and can realise how much more difficult it is to arrest such reactions when occurring at 1000° C. or above without damage to the product; yet such a stoppage must be effected promptly and at precisely the right time, especially in the manufacture of some of the most delicate wares.

¹ The extraordinary success with which the firemen in pottery and other works control the heating within the requisite limits has long evoked the wonder of all who have some understanding of the subject. Considering the thousands of years during which clay has been heated industrially it seems equally remarkable that automatic methods for controlling the temperatures of ceramic kilns have only been in use for a few years.

(b) It may permit the crystallisation of some of the constituents. Thus mullite may be formed in clay goods, cristobalite or tridymite in siliceous materials, periclase in magnesite bricks, etc. In some cases, the production of a mass of felted crystals gives the mass an added strength and a greater resistance to sudden changes in temperature. In others, the crystals are important because they are the most stable form of material under the conditions in which it will be used. In glazes and sometimes in binding materials, the production of crystals is undesirable and is regarded as a defect, though some crystalline glazes are very beautiful.

(c) It may cause the volatilisation of alkalis and thus increase the refractoriness of the residual material, though this can only occur to a very small extent in the soaking stage of burning; it is more important when ceramic products are subjected to prolonged heating at a high temperature during use.

One of the chief purposes of a prolonged finishing stage in the burning of ceramic materials and articles is the production of a suitable amount of vitrified or glassy material which will surround the remaining particles and fill the interstices between them to a suitable extent, dependent on the properties desired in the finished product. In stoneware, engineering bricks, and acid-resisting materials, a large proportion of vitrified material is required so as to fill the pores and prevent the permeation of liquid into the article; in porcelain and china-ware a still larger proportion of vitrified material is needed so as to produce a translucent material without loss of shape. The temperature at which a sufficient amount of vitrification is reached depends on the nature and proportion of the fluxes and of the most fusible materials present. It will obviously be reached earlier with a fusible clay or with one rich in fluxes than with a highly refractory material such as kaolin, magnesite, or bauxite.

Vitrification commences when the fusion point of the least refractory constituents (or of the most fusible product of any reactions which may have occurred) is reached, but owing to the complex nature of ceramic materials no single temperature can be stated as that of the commencement of vitrification. With some very fusible clays and glazes it is as low as 450°C. , whilst some highly refractory materials, such as magnesia and alumina, show no signs of fusion below 2000°C. With most of the crude clays used in the ceramic industries the commencement of vitrification appears to occur at about $750^{\circ}\text{--}800^{\circ}\text{C.}$

A readily fusible substance present in the material may be the first to fuse, but it is more usual for a sodium or potassium salt present as an impurity to decompose and combine with the silica, forming a fusible silicate, which will, as the temperature rises, act as a solvent for some of the other silicates and bases present; the molten material thus forms a liquid in which the various substances can react far more rapidly than when all are in the solid state. By this means, fused complex compounds, eutectics and solid solutions are formed. These changes, which have been described in Chapter X, increase in extent and velocity as the amount of vitrified material increases and the temperature rises, until—unless its progress is previously arrested—a point is reached when there is so much fused material present that the mass is unable to retain its shape and loss of shape occurs, and if the heating is still further continued at a suitable temperature, the whole of the material is reduced to a molten or liquid state and forms, when cooled, a glass or slag.

The rate of vitrification is very slow at low temperatures, but increases rapidly at temperatures above 1200° C. (sometimes at a much lower temperature), except with the most refractory materials, some of which can only be melted in the intense heat of the electric arc.

The chemical changes which occur during the production of vitrified material cause various physical changes to take place simultaneously. Thus, the volume of the material changes as the interstices are filled and the solid material is dissolved, and also as products of different specific gravity are formed. The porosity and permeability decrease as the pores are filled with the molten material. The strength of the hot material decreases as the amount of fused material increases, the mass becoming more mobile, but when cold the strength is increased as a result of the larger amount of fused glassy matter produced acting as a bond uniting the other particles firmly together.

Vitrification is facilitated and the quality of vitrified goods is improved if the body consists of very fine particles, so that for ware of the highest quality the materials are converted into slips and passed through extremely fine sieves in order to separate undesirable coarse particles. The smaller the particles, the more readily do they react and the more smoothly does the vitrification proceed with a consequent reduction in the fuel used in burning and in the wastage through distortion.

Vitrification is also facilitated by the presence of a catalyst or mineraliser, and by any readily fusible substance having strong solvent properties.

The control of vitrification involves not only the gradual production of a fused material, but the retention of the shape of the article as a result of the presence of sufficient refractory particles, so distributed that they act as a skeleton which is not affected by the movement of the molten portion of the body. Unduly prolonged heating will change the properties of the ware by altering the proportion of glass and skeletal matter and the structure of the latter.

The term *vitrification range* is applied to the range of temperature between the commencement of fusion and the loss of shape due to the production of vitrified material. It varies according to the nature of the substances present. Some clays, such as those containing a large quantity of lime or soda compounds have a very short vitrification range on account of the fluidity of calcium and sodium silicates and alumino-silicates; in some such clays the range may be as low as 30° C., whilst in some refractory clays the range may be 300° C. or more. Table XI.IV, due to Wheeler, shows the vitrification range of different clays.

In clays and in some other materials, the vitrification range depends chiefly on the nature of the fluxes present. In siliceous materials bonded by lime or in calcareous or magnesian materials bonded with clay the range will be short, whilst if a moderately refractory clay is used as a bond for a siliceous material, a longer vitrification range will be obtained. Magnesia is usually regarded as producing the longest range of vitrification obtainable with siliceous materials, especially if clay is present, as the product is more viscous than that of the corresponding lime- or alkali-compounds, and as it does not penetrate the pores so readily its rate of attack is much slower. The property does not appear to be present in magnesia-soda glasses which are not more viscous than those in which the magnesia is replaced by lime.

nature of the atmosphere in which they are heated. Thus, chromium compounds are green in a reducing atmosphere, but red or buff in an oxidising one; lead glazes may be blackened in a reducing atmosphere, and manganese and cobalt compounds form bubbles of oxygen if the glaze is heated too long in an oxidising one. Hence, it is impossible to fire all kinds of colours at one time in a kiln. Steady firing is essential for glazes, or the ware may be blistered or 'feathered'. Very slow firing is detrimental to glaze, so that the firing should be as rapid as possible without damaging the ware.

Tables XI.V and XI.VI show the finishing temperatures for various classes of goods.

Refractory articles such as firebricks, crucibles, retorts, etc., should usually be fired at a temperature higher than that at which they are to be used. If this is done, any further heating to a lower temperature cannot have very much adverse effect. In practice, however, it is customary to burn the goods till they are sufficiently hard and have a good 'ring', and it is only within the last few years that the necessity for finishing these articles at a sufficiently high temperature has been properly appreciated.

It is not always necessary to burn firebricks at the maximum temperature reached by the materials in connection with which they are to be used, and in some cases it is impossible to do so, as the bricks, if heated to that temperature, would soften and lose their shape, whereas they are quite satisfactory when only one face or side is raised to that temperature as in actual use. Nevertheless, it is always desirable to burn firebricks at the highest practicable temperature, and it is also important to maintain that temperature for a sufficiently long period (p. 683) in order that the various desirable changes may take place. A mistake which is commonly made is to reach a high temperature, but not to maintain it for a sufficiently long time, the firing being stopped before the heat has had time to penetrate the articles sufficiently.

In *refractory bricks*, there is usually a very small proportion of fused material and to the absence of more is due their refractoriness. The firing of these materials should therefore be such that crystal development reactions are able to proceed; otherwise the ware would have insufficient strength. In practice, a small amount of liquid is desirable at the temperatures at which refractory ware is fired.

Fireclay bricks are frequently finished at about Cone 5a (1180° C.), but this is too low. The better qualities should be fired to Cones 7-12 (1230°-1350° C.), whilst still better ones would be obtained if fired to Cone 14 (1410° C.) or still higher temperatures. In each case, the kiln or oven in which the bricks are burned should be maintained at a temperature within about 50 degrees of the maximum for at least 24 hours so as to ensure a sufficient 'soaking'.

Cooling. When the supply of heat to an oven or kiln containing ceramic articles (or to a furnace or other structure of which they form a part) ceases, the articles gradually cool down. The heat will be lost slowly if the kiln or oven is tightly sealed, but it may be withdrawn rapidly by passing a sufficient quantity of cold air through the chamber. The latter will usually destroy the goods by causing them to crack and disintegrate, as most ceramic materials, when fired, are sensitive to sudden changes in temperature. To avoid damage, it is necessary to ascertain what are the best conditions for cooling. These naturally differ with the nature of the product, but, as a general rule, the more porous the material, the more rapidly can it be cooled

TABLE XI—V. FINISHING TEMPERATURE FOR BUILDING BRICKS, TILES, ETC.

<i>Type of Ware</i>	<i>Finishing Temperature</i>	
	<i>Seger Cone</i>	<i>° C.</i>
Red bricks, and tiles rich in iron and lime	015a-01a	790-1080
Red bricks, and tiles free from lime	1a-10	1100-1300
Glazed bricks	6a-9	1200-1280
Staffordshire blue bricks	10-14	1300-1410
Clinkers and pavours	1a-10	1100-1300
Vitreous tiles	5a-6a	1180-1200
Salt-glazed bricks, drain pipes, etc.	5a-10	1180-1300

TABLE XI—VI. FINISHING TEMPERATURES OF EARTHENWARE, ETC.

<i>Type of Ware</i>	<i>Finishing Temperature</i>	
	<i>Seger Cone</i>	<i>° C.</i>
Whiteware, biscuit	3a-10	1140-1300
Whiteware, glost	01a-10	1080-1300
Easy earthenware, biscuit	4a-5a	1160-1180
Hard earthenware, biscuit	5a-6a	1180-1200
Easy earthenware, glost	03a-1a	1040-1100
Hard earthenware, glost	2a-3a	1120-1140
White stoneware (soft glaze)	09a-03a	920-1040
White stoneware (hard glaze)	1a-10	1100-1300
Stoneware with salt glaze	5a-10	1180-1300
Stoneware (chemical)	6a-12	1200-1350
Majolica ware	015a-05a	790-1000
China biscuit ware	9-10	1280-1300
Soft porcelain ware	8-10	1250-1300
Hard porcelain ware	7-20	1230-1530
Hard porcelain glaze	13-16	1380-1460
Glass colours	022-021	600-650
Easy enamel kiln	020-018	670-710
Medium enamel kiln	017-016	730-750
Hard enamel kiln	016-015a	750-790
Porcelain colours and lustres	022-010a	600-900

with safety. Glass, porcelain and other articles containing a large proportion of vitreous matter, on the contrary, must be cooled skilfully, and it is usually necessary with such materials to vary the rate of cooling at different temperatures; this variation or control of the cooling is known as *annealing*. Unless the proportion of vitreous matter is large it is usually possible and desirable to allow the ware to cool rapidly from the finishing temperature to about 900° C., but below the latter temperature the cooling must usually be much slower, and even above it an excessive rate of cooling may be dangerous with large, thick pieces of highly vitrified ware.

Many fused and vitreous materials tend to crystallise if maintained too long at a temperature above 900° C., so that rapid cooling through the 'crystallisation zone' is

essential where a vitreous structure is desired as in glazes and in most ceramic ware. Such crystallisation may be beneficial or objectionable according to the crystals formed. If the crystals form a felted mass (e.g. mullite) they act as a reinforcement to the glassy matter and produce very strong ware (e.g. porcelain and stoneware). Isolated crystals and those arranged in small bundles like faggots are a source of weakness rather than strength. In glazes, the formation of crystals is usually regarded as a defect (*devitrification*), but occasionally they are considered to be decorative, as in *crystalline* and *aventurine glazes*.

The formation of the crystals is due to the fact that, when sufficiently heated, all silicates, aluminates, and alumino-silicates are soluble in each other, but when the temperature changes some of the products become insoluble, and are thrown out of solution in the form of crystals. Thereby, a new series of compounds is gradually formed, with properties very different from those of the original materials, though the chemical composition of the whole, as shown by analysis, may remain unchanged. To this extraordinary change in the properties of the finished product many ceramic materials owe their unique value.

Cooling the kilns improperly is a fruitful source of many defects, especially 'crazing', 'cracks', 'dunts' and 'feathering' or crystallisation, and great skill and care are needed to avoid them.

The few investigations which have been made on the effect of cooling ware at different rates during various stages of cooling show that there is scope for a very careful study of this subject. At present there is not sufficient information for any precise statement to be made on the various rates which should be adopted; they appear to differ with each class of ware.

In order to avoid certain defects, it is customary to raise and lower the temperature of kilns containing clay-ware very slowly. In many works, bricks, tiles, and terra-cotta do not attain the maximum temperature in less than ten days (i.e. 240 hours) and a further six days or more is allowed for cooling. Pottery and other hollow-ware can be heated and cooled much more rapidly, but for much of it more than 168 hours is allowed. These very low rates are partly due to the limitations imposed by the kilns employed and investigations on a laboratory scale have indicated that much more rapid rates of burning are practicable. With the advent of tunnel kiln methods of firing, the burning cycle of some types of glazed ware can be reduced to 60–80 hours. Unless great care is exercised during firing under such conditions, the quality of the ware will be inferior to that produced from slower fired kilns. It is important that the ware entering rapid-cycle tunnel kilns should be perfectly dry and that the temperature gradients should be so adjusted that an excessive rate of change of temperature is avoided during critical stages in the firing. Clays with a high content of free quartz and those containing carbonaceous matter cannot be burned rapidly without developing serious faults.

In such kilns, bricks, tiles and pottery can be fired, cooled and drawn in 48–72 hours, whereas in an intermittent or Hoffmann-type of continuous kiln two or three weeks would be required.

Some decorated, glazed wares must be fired several times because some of the colours used are spoiled by overheating and because some glazes cannot be applied to unfired ware. This use of *two or more firings* was first introduced into England by

Enoch Booth of Tunstall, Staffs. (about A.D. 1750); he fired a white stoneware body and produced *biscuit ware* which was then glazed and re-fired at a lower temperature, producing *glost ware*. In *coloured or decorated ware*, each colour may require a different temperature, so that they must be applied in an order of diminishing temperatures, with a separate firing after each application. The position in which decorated articles are placed in a glost-oven is very important and much skill and experience are needed to ensure the correct setting of such wares.

THE COMPOSITION OF FIRED CLAYS

THERE are two entirely distinct phenomena occurring in clays heated at high temperatures. These are (a) crystal formation due to the recombination and recrystallisation reactions, and (b) liquid formation. This latter material may crystallise on cooling, but siliceous melts are prone to supercool and often 'freeze' to a homogeneous glass or a partially crystallised system.

The relative rates of crystal formation and of liquid development in a particular clay cannot be predicted because of the complexity and number of factors involved. The composition, grain-size and distribution of minerals, firing rate and maximum temperature all contribute to both types of reaction and, in addition, the two phases may mutually interact after they have been produced. Thus the liquid which develops during firing may dissolve some of the crystals formed by solid reaction processes and, conversely, some liquid may crystallise on contact with the solid by reason of the change in composition produced, or by the 'seeding' of a supercooled phase.

The rate at which the fired body is cooled may have a pronounced influence on the final product. Some crystalline phases may invert or convert at a particular temperature and changes in composition may occur in minerals which form solid solutions (see p. 557). The liquid phase undergoes the greatest change, however, because, on cooling it solidifies.

The liquid in clays which have been heated to high temperatures is invariably rich in silica. Associated with this acidic component are the basic constituents such as sodium, potassium, iron, magnesium and calcium oxides which were originally present in the clay and associated minerals. In addition, aluminium and, to a lesser extent, titanium may also be constituents of the liquid phase on firing. When such liquids are cooled, a glass or supercooled liquid tends to form by the freezing of the silica network in a random manner. The factors which influence glass formation have been outlined in Chapter X and these may be summarised as:

- (a) The rate of cooling.
- (b) The viscosity of the liquid in the temperature region of incipient crystallisation.
- (c) The composition of the liquid.

Crystallisation in silicate melts is usually slow and consequently a rapid rate of cooling may inhibit the appearance of a crystalline phase which under slower rates of decreasing temperature might crystallise completely.

Some silicate melts are viscous even at high temperatures—particularly when

magnesium oxide is the principal fluxing element. Such mixtures do not crystallise readily because the free movement of the ions or atoms of the liquid is retarded and they are unable to rearrange to form an ordered crystalline lattice. Other elements, for example the alkali metals, form liquids which do not crystallise until the temperature is below 700° C., and the viscosity is invariably high. These mixtures crystallise only with extreme difficulty and readily form glasses.

The effect of composition on the tendency to form glasses has been investigated by Zachariasen, Stanworth and others and has been described in Chapter III. Glass is more liable to form when the silica content is high but it becomes progressively less stable as the amount of elements which may replace silicon as a network-former is increased. Liquids with a high proportion of alumina will crystallise more readily and, all else being constant, will be less liable to produce glass than those more rich in silica.

This is one of the most important principles governing the composition of fired clay products, because irrespective of the amount of liquid formed on firing, the proportion of glass in the cooled mass will be governed by the ease of crystallisation.

Fired clay mixtures which are low in alumina and high in silica will contain more glass on cooling than those with a higher proportion of alumina, even though the fluxing elements, firing temperature and cooling rate are kept constant in both cases.

As the glassy phase must be derived from a parent liquid, the amount which is present in a vitreous body will depend on the extent of liquid development under the particular firing conditions. It is, therefore, to be expected that, in addition to the temperature and rate of heating, the amount and availability of fluxing elements contribute to the proportion of glass in the cooled ceramic material.

The changes in composition which determine the constituents of a clay when it is fired and then cooled may be summarised as:

(a) Decomposition reactions occurring at comparatively low temperatures (p. 657).

(b) Primary crystallisation through reactions proceeding in the solid state (p. 661).

(c) Liquid formation which on cooling forms:

1. glass or
2. secondary crystallisation products.

Inferior or low-grade clays are usually rich in fluxing elements principally of the alkali type and have a high silica content, due to the proportion of sandy constituents. With such compositions, liquid forms in large amounts even at relatively low temperatures and it does not crystallise readily on cooling. *Building bricks, roofing tiles, terra-cotta ware*, and similar materials are principally composed of a crude glass which surrounds isolated crystals mainly of unchanged quartz. Primary crystallisation products (except mullite) are rarely detectable because, if they form at all, they are quickly dissolved in the liquid phase. Secondary crystallisation is not extensive especially when the fluxing elements are principally alkaline. Bricks rich in lime occasionally contain feldspar produced by crystallisation from the liquid during the cooling.

Clays with a higher content of alumina usually contain a lower content of fluxing elements than those which are suitable for building brick manufacture. Consequently, less liquid will form under the same heating conditions and the proportion of glass will not be as great. More primary crystallisation products, principally mullite and cristobalite, will be present.

The *fireclay* series is an excellent illustration of the effect of composition on the fired product; the alumina content extends from about 20 per cent to 80 per cent or more, silica being the other major constituent. The fluxing elements are usually less in amount in highly aluminous clays, although this is not so in all cases. The amount of glass in the final refractory bears some relationship to the content of fluxing elements, but is more closely associated with the proportion of silica. Fired clays low in alumina are comparatively rich in glass but, as the proportion increases, the liquid phase produced at high temperatures more readily crystallises on cooling to form mullite.

Bricks made from *highly aluminous clays* contain corundum (α -alumina) and mullite as primary crystallisation products. Surrounding such grains the remains of a liquid phase can often be observed, but this has largely crystallised on cooling, mainly to mullite, leaving only small amounts of an amorphous glassy phase.

When fluxing elements are absent or small in amounts, as in purified kaolinite, the fired products are solely primary crystallisation phases which, in the example quoted, will be mullite and cristobalite or tridymite.

The *silica minerals* are commonly present in fired clay bodies. Quartz is frequently a principal mineral in clays and unless the temperature of firing is excessively high it does not convert to cristobalite or tridymite to a great extent. This change is slow at temperatures below 1250° C., especially when alumina is present to act as a retarder (see p. 629). Flinty or chalcedonic particles of silica associated with sedimentary clays are readily converted at about 1250° C. and are usually changed on firing to one of the more stable crystalline forms of silica. Free silica is rapidly attacked by alkalis or liquids rich in alkalis and is dissolved in the melt.

Cristobalite and tridymite are often formed by recrystallisation of amorphous silica in the region of 1250° C., and they are therefore primary crystallisation products if the liquid phase is small in amount. Both these forms of silica may also crystallise from a siliceous melt on cooling and will do so when the liquid has become supersaturated with silica through the solution of quartz and other forms of free silica in the clay.

A fired clay or clay product may thus range in composition from the extremes of an entirely glassy composition to a completely crystalline mass. In most cases, there will be partly glass and partly crystalline matter, but the relative proportion of each is all-important in determining the properties of the product as will be demonstrated in the next chapter. Mullite and the silica minerals are the principal crystalline components in all well-fired clay bodies, though corundum may be present in high alumina products. Mullite with its habit of forming needle-shaped crystals can produce an interlocking, intergrowing network which confers high stability and strength at elevated temperatures—an invaluable property in some clay products.

The relative amounts of glassy and crystalline phases can be controlled by the temperature and duration of firing and by altering the composition of the raw body.

Thus, an entirely vitreous body can be produced by adding the correct proportion of sodium, potassium, calcium or other flux either in the form of bone ash, felspar, nepheline, whiting or similar substance. The production of an almost wholly crystalline body is not so easy, because the minerals containing fluxing elements are not readily removed from the raw body by mechanical means. Increased crystallinity can be secured, however, by additions of alumina prior to firing.

The manufacturer of clay-ware has to arrange the kiln firing cycle so that the most desirable properties in the fired material are retained and to do this the correct balance must be achieved between crystallinity and glassy bond.

Clays for the manufacture of *building bricks* and *allied products* usually contain sufficient fluxes, e.g. soda, potash and lime, to develop an appreciable glassy phase even at low firing temperatures and the resulting products are hard and dense and sonorous when struck. Too much vitrification is undesirable, as it may lead to warping and excessive shrinkage (see Chapter XII). Furthermore, when a brilliant red colour is required the firing must be finished before much vitrifiable material has been formed, as this tends to produce an unpleasant brown instead of the brilliant terra-cotta colour which is so much desired in some clay products.

Coarse Earthenware and *Terra Cotta* are made from clays which have a similar composition to those used in the manufacture of building bricks, but they are usually more finely ground. They must vitrify at about 1150° C. to give a strong body when cold, but the firing shrinkage should not be excessive. Such bodies, therefore, contain a proportion of pre-calcined material, termed 'grog' or 'pot', the amount of which is usually between 15–30 per cent. The grading of the body (p. 377) should be carefully adjusted.

Faience has a similar composition but is of finer grain-size than earthenware; the body which may contain a high proportion of 'grog', is crushed to pass a 30-mesh screen. The clays used in the manufacture of faience usually burn white or near white.

Fine Earthenware is made from white-burning clays (kaolins and ball-clays) with felspar or Cornish stone and flint. It is burned at a temperature where liquid is formed which supercools to a glass sufficient in amount to impart strength but giving a porous body.

A high proportion of the fired body is crystalline, the predominant minerals being cristobalite and mullite. The liquid may partially crystallise on cooling forming various silicates and alumino-silicates, the chief of which is felspar.

Stoneware bodies have a similar composition to coarse earthenware but they are fired to a higher temperature to produce a predominantly glassy, impervious body. The glass, which is highly siliceous, fills the voids between crystals of unchanged quartz, cristobalite and mullite.

China ware and *Porcelains* vary considerably in composition (p. 334). Soft porcelains closely resemble opaque yet translucent glasses. A glass of high melting point is incorporated as a frit and the other ingredients fuse at the temperature of firing and form an impervious body. The particles of frit provide a skeleton which prevents excessive liquid formation and consequent distortion. The amount of crystalline material in soft porcelain is very small.

Hard porcelains contain a much greater amount of crystalline phase than do soft

porcelains, although in most commercial porcelains, the proportion rarely exceeds 35 per cent.

The changes on firing in a hard porcelain body are such that the body consists of a felted mass of crystals that are mainly mullite and these form a skeleton throughout the body, the voids of which are filled with glass which may be partially crystallised to mullite or feldspar.

The changes on heating and the fired composition of *bone china* have been studied by St. Pierre.¹ Little change other than the evolution of water and carbon dioxide occur up to about 1000° C., but above this temperature the bone ash begins to decompose giving β -tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$). The lime which is liberated during this reaction combines with the clay body to form anorthite. A highly fluid liquid is formed which reacts with other raw ingredients and gradually dissolves them—quartz is least readily attacked but in well-fired bone china no free quartz can be detected. The final phases on cooling are β -tricalcium phosphate, anorthite and glass, the amounts of which are determined by the proportions of bone ash and lime in the raw materials of which the body is composed.

The composition of other ceramic materials including steatite, cordierite, rutile and zircon bodies have been described in Chapter VI.

In *glazed ware manufacture* the correct temperature conditions during the glost-firing must be maintained to permit the fusible layer of glaze to react partially and adhere to the clay body, but excessive fluidity must be avoided.

Fireclays and other *refractory clays* required to withstand high temperatures, should have a minimum of glassy phase, because a crystalline body is much better able to resist deforming stresses under operating conditions. Hence the firing must be adjusted to yield the precise properties required.

From the foregoing it will be seen that in burning ceramic articles made from clay, crystalline components and a liquid phase form simultaneously at speeds governed principally by the composition of the body and rate of temperature rise. The liquid phase, especially at high temperatures, becomes dominant, dissolving the crystalline products, permeating the mass and eventually, if the heating were sufficiently prolonged and intense, the whole of the material would change into a molten liquid.

As this would involve complete destruction of the article, the reactions which occur must be arrested at a point at which sufficient vitreous material has been formed to impart to the article (when cold) the desired properties, of which the chief are usually the strength and porosity, though other properties dependent thereon, such as resistance to acids as well as other independent properties, may require to be considered in determining the finishing temperature and the duration (if any) of the soaking period. Thus, if colour is of great importance, as in some pottery and terracotta, the finishing temperature must be low and the proportion of vitreous material small; if the strength of the product is to be the predominant property, the finishing temperature must be higher and the soaking period prolonged so as to produce a larger proportion of vitrified material; whilst if complete impermeability, resistance to acids, hardness, or translucency, or any of these are to be predominant, the finishing temperature must usually be very high and the duration of the soaking very

¹ St. Pierre, P. D. S., *J. Amer. Ceram. Soc.*, 38, 217, 1955.

prolonged in order that the reactions which produce the fused vitreous material may proceed as far as possible without causing loss of shape in the product.

To anyone acquainted, even to a minor degree, with the nature of the reactions involved and the necessity of arresting them at precisely the right time, the firing of porcelain and some other forms of ceramic ware, under the conditions and with the restrictions imposed in commercial work, must be a continual source of wonder. Were we less accustomed to it we should find it difficult to believe that such complex reactions could be controlled so effectively, with such crude and imperfect means as are used regularly in the manufacture of earthenware, china-ware, and other pottery of the highest quality. In probably no other industries does the art of controlling chemical reactions, whose very nature is largely unknown, rise so high as in the firing of ceramic wares.

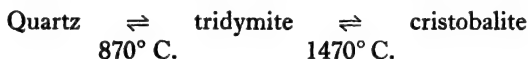
CHANGES IN COMPOSITION ON FIRING SILICEOUS MATERIALS

SILICA may exist in a variety of crystalline forms, each of which is stable over a fixed range of temperature as described in Chapters III and X.

Two quite distinct types of thermal change are associated with the changes in the silica minerals; these are (a) conversions, and (b) inversions.

Conversions involve a pronounced change in crystal type (sec p. 163); they proceed at a sluggish rate and, although reversible, the change takes place so slowly at the critical temperature that it is not observable under ordinary conditions.

The stability ranges of the minerals have been quoted by Fenner¹ as



The transformation of quartz is not as simple as the above scheme suggests, nor is that of tridymite to cristobalite.

The changes are so slow that pure quartz can be maintained at temperatures well above 870° C. without pronounced change and, once the high temperature varieties are formed, they can be cooled and maintained at room temperature for an indefinite period of time without reconvertng into quartz.

Pure quartz crystals are highly stable even at temperatures well above 870°. Grimshaw, Hargreaves and Roberts² have measured the amount of Madagascar crystal which is decomposed at various temperatures after long periods of firing. Their results are summarised in Table XI.VII.

The critical temperature for the change was deduced by assessing the rate constant at various temperatures and extrapolating back to zero conversion. The initial product of the decomposition of quartz is probably a transitional, unstable entity which then slowly reverts to one of the other crystalline modifications. Almost invariably cristobalite forms in preference to tridymite even in the temperature range of stability of the latter mineral. It is only after prolonged firing that

¹ Fenner, C. N., *Amer. J. Sci.*, 36, 331, 1913.

² Grimshaw, R. W., Hargreaves, J. and Roberts, A. L., *Trans. Brit. Ceram. Soc.*, 55, 36, 1956.

tridymite appears as a product of heating pure quartz and unless some catalytic agent is present the change may take a geological age if it proceeds at all.

Silica brick manufacturers must ensure that the firing is sufficiently intense to destroy as much as possible of the quartzitic material in the raw silica rock and convert it into tridymite or cristobalite. Only by this means can bricks be produced which are stable and free from further large volume changes (see Chapter XII) when in use.

Fortunately, the slow change of crystalline type can be greatly accelerated by catalytic agents (see p. 165). Many materials are suitable and have been employed; some promote the formation of tridymite whilst others accelerate the production of cristobalite, and the reaction can proceed either entirely in the solid state or through the medium of a liquid phase.

TABLE XI—VII. THE PERCENTAGE
DECOMPOSITION OF PURE MADAGASCAR QUARTZ CRYSTAL
AFTER FIRING AT DIFFERENT TEMPERATURES

Firing Temperature	1270° C.		1320° C.		1370° C.		1450° C.	
Grain-size range* B.S.S.	- 100 + 120	- 240 + 300	- 100 + 120	- 240 + 300	- 100 + 120	- 240 + 300	- 100 + 120	- 240 + 300
Firing time (hours)								
1	0	0	0	0	0	0.3	1.0	9.8
2	0	0	0	4.1	0	4.1	1.9	16.8
4	0	0.7	0	4.5	0.4	6.7	9.7	44.1
12	0	2.3	0	7.2	1.5	16.8	59.5	80.0
24	0.2	3.6	0.2	14.9	7.5	29.2	83.6	95.5
48	0.4	6.2	0.6	25.9	27.4	49.3	100	100
96	1.0	13.5	3.5	45.1	55.5	87.2	100	100
240	8.7	28.0	61.5	80.0	92.0	100	100	100

* The centre grain-sizes of the two fractions were 0.138 mm. and 0.053 mm. respectively.

The mode of action of the solid state catalysts, or *promoters*, appears to be the establishment of nucleated surface regions where contact occurs with a quartz grain. These rapidly spread until the whole particle is decomposed when reaction either stops, or under favourable conditions continues into other grains in contact with the first (see p. 629).

When a liquid phase is capable of being formed between the catalyst and silica at the temperature of firing, the activity or rate of decomposition is greatly increased as the mobility of the promoter is greater when in the liquid form.

Many attempts have been made to explain the fundamental mechanism of the catalytic behaviour. In some, the size and electrical nature of the cation of the promoter have been regarded as all-important. This is by no means a complete explanation, because the anionic component may also influence the change. Potassium oxide for example, or the corresponding tungstate or phosphate are extremely rapid in action, whilst potassium chloride added in the same molecular amounts is much less effective. In a similar way, the rate of change in the presence of some catalysts is

influenced by the atmospheric conditions inside the kiln or furnace. Reducing conditions or an excess of carbon monoxide assist the change, although nitrogen has the opposite effect.

Salts of the alkali metals (lithium, sodium and potassium) are the catalytic agents which, in general, produce the most rapid changes. This is to be expected, as these components combine readily with silica, even at low temperatures to form a mobile liquid. Iron oxide is another commonly-occurring material which forms a eutectic with silica at comparatively low temperatures and it too is an energetic catalyst. Lime and magnesia react entirely in the solid form, but are quite active especially in the initial stages of firing (see p. 165).

Alumina is anomalous in behaviour because it not only fails to catalyse the decomposition of quartz, but retards the reaction and furthermore inhibits the activity of other normal catalysts when it is mixed with them.

Titania is of doubtful behaviour; under oxidising conditions it is a weak catalyst, but, in a reducing atmosphere, it may exert a retarding influence, but to a lesser extent than alumina.

Relatively small amounts of a catalyst are required to cause conversion, especially if a liquid phase is formed during the heating. When the reaction proceeds entirely in the solid state, however, the rate of reaction depends mainly on the contact points between the catalyst and the quartz, hence the speed of the change may be increased by adding larger quantities of the promoter.

The relative effect of various oxide catalysts on the decomposition of quartz is shown in Table XI.VIII. The amounts added in each case were calculated to give the same number of contact points for reaction between the quartz and oxide (see p. 629). The particle-number ratios of quartz to catalyst were about 200:1 in all cases which corresponds to an addition of about 1 per cent of oxide in each case. Three additions of calcium oxide are included, with progressively increasing amounts, to show the effect of concentration.

The alkali oxides cannot be included in the Table because at 1370° C., quartz is completely decomposed in their presence in a few minutes. Even at 1100° C., 1 per cent of either sodium or potassium oxide will completely convert quartz of the same grain size in four hours.

The temperature of heating also influences the rate of reaction in the presence of catalysts in much the same way as with pure quartz.

It is of great importance that when the added promoter does not form a liquid but catalyses entirely in the solid state, the reaction is rapid only in the initial stages of kiln firing and eventually, if there is an insufficient supply of the accelerating agent, the rate falls to that of pure quartz (see p. 629). This is related to industrial practice—where the normal addition is milk of lime; the bulk of the quartz is rapidly converted (as shown by density measurements), but the final traces can only be transformed after prolonged firing at a very high temperature. Should alumina be present, even in small amounts, the rate of conversion is much less and as this component has other undesirable influences on the properties of the finished bricks, quartzites with the minimum quantity of alumina are preferred.

In addition to markedly influencing the conversion rate, catalytic agents also determine, to a large extent, the nature of the product formed.

The alkali metals, especially when combined with highly polarisable cations such as phosphate or tungstate, favour the production of tridymite. These are the only agents which are accepted generally as tridymite promoters, although it has been claimed that iron oxide added as boiler scale behaves similarly. Whilst it is true that silica bricks rich in tridymite can undoubtedly be produced by the addition of 5 per cent of this material, it is a matter of conjecture whether the catalytic influence should be attributed to the iron oxide or the alkali salts which are also present in boiler scale.

Most other oxides or compounds either catalyse the formation of cristobalite or do not influence the conversion of quartz to any appreciable extent.

TABLE XI—VIII. THE PERCENTAGE
DECOMPOSITION OF MADAGASCAR QUARTZ CRYSTAL IN THE
PRESENCE OF VARIOUS CATALYSTS AT 1370° C.

Mixture	Particle No. Ratio quartz:catalyst	Time of firing (hours):					
		$\frac{1}{2}$	1	2	4	8	16
Pure quartz		1.0	3.0	4.0	6.5	11.0	20.0
+ Fe ₂ O ₃	200:1	11.9	15.7	24.9	38.0	62.7	95.4
+ CaO	200:1	13.9	20.8	25.0	27.4	30.2	39.7
	100:1	20.0	32.6	41.3	47.4	51.2	59.3
	50:1	30.0	41.9	50.2	59.5	63.9	80.0
+ CaO + Al ₂ O ₃	200:1:1	5.5	13.1	18.6	22.7	26.5	28.5
+ Al ₂ O ₃	200:1	1.0	3.0	4.5	6.5	6.5	7.4
+ MgO	200:1	5.0	10.0	17.5	21.5	25.5	33.5
+ TiO ₂	200:1	4.2	10.0	18.2	20.5	25.0	30.0

The grain-size of quartz was in all cases - 100 + 120 B.S.S.

The alkali earth oxides are particularly efficient as catalysts and as they do not produce a liquid phase with silica at the temperatures of firing and service, they are the catalysts most commonly employed in the manufacture of high-grade products. Calcium oxide (as milk of lime) is frequently used in amounts up to 2 per cent. The commercial use of barium salts as catalysts in India has been reported.

The raw materials used in the manufacture of silica and siliceous refractories differ from pure quartz crystals in composition and texture and their firing characteristics are correspondingly different. Silica occurs in Nature in a variety of forms (see Chapter VI), which include the truly amorphous types, such as opal, and crypto-crystalline varieties (of which flint and chalcedony are examples), in addition to crystalline quartz. Natural quartzites are mixtures of these various forms and the relative proportions determine the nature of the material and of the fired product.

The true amorphous silica minerals are of extremely small particle-size—in fact, the ultimate grains may be of molecular size. Crypto-crystalline material is thought to be composed of particles of quartz of submicroscopic size; X-ray and thermal tests indicate that the proportion of true quartz in them may be as low as 20 per cent, but whether this is the result of the extreme fineness of the particles or to associated colloidal material is not clearly established.

Crystalline quartzites are those with larger grains easily detectable under a microscope, but many samples contain associated flint or chalcedonic grains and most show evidence of secondary silicification (see Chapter I) indicating a proportion of amorphous or non-quartzitic material.

All the naturally-occurring siliceous materials contain small proportions of a wide variety of minerals present as impurities. Sericite or hydrous mica is common in British silica rocks and this is usually the source of alumina in the material. Silcrete, a crypto-crystalline silica rock, mined in Germany, Italy and South Africa frequently contains up to 5 per cent of titanium-bearing minerals.

On firing, such materials are converted to the high temperature modifications but, usually at a far faster rate than are crystals of pure quartz. This is mainly because of the smaller particle-size and the presence of colloidal or crypto-crystalline material which changes rapidly and then acts as 'seeds' for the reaction of the more crystalline varieties. The presence of an amount of such rapidly-converting material is probably essential if a quartzite is to be suitable for the manufacture of siliceous refractories. Pure quartz reacts too slowly under commercial conditions; but, on the other hand, an excess of amorphous silica is also unsuitable. So rapidly does this substance convert that a shape prepared from it may be shattered by the excessive rate of change in volume on heating. Under fairly rapid heating conditions, the transformation in amorphous silica may be detected by observing the thermal change at about 1250° C.

Quartzites of good quality may contain up to 98 per cent silica, but the small percentage of impurity minerals is sufficient to produce an appreciable amount of liquid on firing. This is augmented by the action of the catalyst or promoter added to the raw material to accelerate the rate of conversion. *Lime* or *iron oxide* (the two principal additives) do not readily form a liquid with silica, but the presence of a small proportion of alumina is sufficient to cause fluidity at a kiln-firing temperature of 1450° C.¹

Ford² has calculated the proportion of liquid which can form in silica mixtures when fired to various temperatures. The effect of varying amounts of alumina on the liquid formed by 2 per cent additions of lime and magnesia is shown in Table XI.IX.

Most of this liquid which is produced on firing becomes a glass on cooling which surrounds the crystals of cristobalite and tridymite which have formed. The properties of this glass are, however, unusual and it may be that, as it is highly siliceous, a structure can be induced in it by the embedded silica crystals.

Alumina when present in siliceous materials, not only gives rise to undesirable liquid formation at high temperatures but also inhibits the degree of conversion. This is especially noticeable in siliceous clays where even at high temperatures and on prolonged heating, quartz grains are converted only slowly to one of the high temperature varieties of silica. Quartz can often be detected in fireclay refractories which have been in constant service at temperatures over 1250° C. for periods of many years.

¹ It has been estimated that 1 per cent of alumina in a quartzite is sufficient to produce 10 per cent liquid in a brick at a temperature about 1620° C. in the roof of a basic open-hearth furnace.

² Ford, W. F., *Refract.*, 33, 76, 1957.

Crypto-crystalline quartzites usually contain a higher proportion of impurities than the more coarsely grained varieties, yet, for reasons which have not yet been definitely established, the amount of liquid formed on firing is not as large as would be expected from their composition. This may be due to the rapidly-inverting material trapping the impurities which are more evenly distributed than in the coarse-grained varieties. The liquid is thus limited to small isolated pockets and is not able to disseminate throughout the body as when a coarse material is used.

Silica bricks must be fired to ensure that all the quartz has been converted and that no further change will occur in service. Those of the best quality ought to be fired at Cones 14–18 (1410–1500° C.), including a soaking period (p. 670) at or near the maximum temperature of at least 8–10 hours.

TABLE XI—IX. THE PROPORTIONS OF
LIQUID FORMED IN MIXTURES OF SILICA WITH
ALUMINA AND LIME OR MAGNESIA

	2 per cent lime			2 per cent magnesia	
	<i>Alumina (per cent)</i>	1·00	0·67	0·30	
1400° C.		9·4	8·0	6·4	7·0
1500° C.		11·6	9·3	7·4	9·1
1600° C.		16·7	12·0	9·0	10·0
(1650° C.)		(40)	(23)	(16)	(20)
1700° C.		85	60	30	60

The figures in brackets are estimated values.

At temperatures slightly in excess of 1700° C., the crystalline modifications of silica melt into a highly viscous fluid. Pure quartz, if heated in the absence of air, can be melted without excessive conversion at 1690° C., tridymite similarly at 1710° C., whilst cristobalite (the most stable phase) requires to be heated to 1725° C.; in each case the product is virtually identical. Once liquefied, silica does not readily recrystallise and can be supercooled to form a glass which is known commercially as *fused silica*. This can be 'devitrified' or recrystallised by prolonged heating above 1200° C. when cristobalite forms.

Although, after suitable firing treatment at about 1450° C., little or no quartz remains in silica refractories, the combined proportions of tridymite and cristobalite may not be greater than 50 per cent and rarely exceed 75 per cent. Quartz is converted into an intermediate, unstable form of silica from which cristobalite develops. If promoters which catalyse the formation of tridymite are present, the primary cristobalite, in turn, is converted into a transitional phase from which tridymite crystallises.¹ This succession of changes is slow and the catalysts and promoters tend to become exhausted as the reactions proceed. Consequently in fired silica bricks, it is usual to find a considerable amount of non-crystalline silica over and above that which could be present as a glass. Firing at high temperatures (*circa* 1650° C.)

¹ Gaskell, J. A., Grimshaw, R. W. and Roberts, A. L., *Gas Research Board Publication* 1956.

causes the amorphous silica to crystallise as cristobalite¹ and it may well be that the remarkable ability of silica refractories to withstand temperatures to within a few degrees of their melting point is due to this effect which increases the proportion of crystalline components by as much as 30 per cent.

Inversions. The silica minerals each undergo additional changes when heated which do not involve a pronounced change in crystallographic form (see p. 164). These small rearrangements in structure are termed *inversions* and take place at well-defined temperatures. In contrast to the conversions these reactions are rapid and instantaneously reversible.

They may be summarised as:

Quartz	$\alpha \rightleftharpoons \beta$	573° C.
Cristobalite	$\alpha \rightleftharpoons \beta$	210–280° C.
Tridymite	$\alpha_1 \rightleftharpoons \beta_1$	116° C.
	$\alpha_2 \rightleftharpoons \beta_2$	163° C.

It is now known that quartz inverts over a short range of temperature although in most cases it occurs within a degree of 573° C. The variations in the inversion temperature are attributed by Keith and Tuttle² to possible defects in the structure or the incorporation of foreign ions. The variability of the inversion temperature of cristobalite is most probably due to a similar cause. The higher the temperature and the longer the duration of firing, the higher is the inversion temperature of cristobalite, but, the presence of foreign ions also exerts a marked influence; thus, sodium catalyses the formation of cristobalite from quartz and the material so produced after heat treatment at 1350° C. inverts at 268° C. Under the same conditions, calcium, magnesium and other cations form cristobalite with an inversion at 232° C.; but cristobalite formed on heating pure kaolin at 1250° C. has an inversion point at about 216° C.

The inversion effect may be measured by the small thermal change which accompanies the reaction; the total heat change is about –2.8 calories per mole and the reaction is thus an endothermic effect on heating but, on cooling, is exothermic, i.e. will liberate heat.

Cristobalite prepared in different ways is frequently different in thermal behaviour; the presence of magnesium gives a cristobalite in which the inversion is sharp and the heat is liberated over only a small range of temperature; lime and, to an even greater extent sodium compounds catalyse the formation of a form which inverts over a range of up to 10° C.

The range of temperature in the inversional effect of cristobalite samples is due to many individual crystallites which each invert instantaneously but at different temperatures. Chaklader and Roberts³ have demonstrated this fact by cine-microphotography on a thin-section of a silica brick which was slowly heated or cooled through the inversional range of cristobalite on a hot-stage microscope; the change from $\alpha \rightleftharpoons \beta$ cristobalite in a crystallite was accompanied by an instantaneous increase in transparency.

¹ Chaklader, A. S. and Roberts, A. L., private communication.

² Keith, M. L. and Tuttle, O. F., *Amer. J. Sci.*, Bowen Vol., Part 1, 203, 1952.

³ Chaklader, A. S. and Roberts, A. L., *British Ceram. Soc.*, Autumn Meeting, 1956.

Tridymite is unusual in having inversions at two temperatures but it is probable that two forms of the mineral exist each of which occurs in both the low/high or α/β varieties; the difference in type may be due to solid solution. Tridymite formed from pure quartz by firing with potassium oxide for short periods at 1350° C. exhibits only the lower inversion effect. Prolonged firing increases the magnitude of the change at 163° C. until eventually it approaches in size that at 116° C. which has progressively diminished.

The amorphous varieties of silica have no inversion effects and the crypto-crystalline types show the quartz change on a very reduced scale. Finely-ground quartz crystals have an inversion effect which is very much less than that in the untreated material. This is due to the production of a distorted surface layer in which the configuration of quartz has been destroyed.

High temperature or β -cristobalite has been reported as existing in a metastable condition at room temperatures. In partially devitrified siliceous glasses, a crystal form has been detected which gives an X-ray pattern corresponding to the theoretical spacings of β -cristobalite. It has been postulated that the surrounding glass phase exerts a restraining influence on the crystal and prevents the inversion. β -quartz may also exist in the metastable form when silica glass is devitrified at temperatures below 870° C.

The stabilisation of the high temperature forms is not of common occurrence, however, and they are readily destroyed by prolonged heat treatment and by fine grinding.

The Composition of Silica Refractories. A silica brick of good quality must contain less than 1 per cent of alumina and a total alkali content of less than 0.2 per cent. Calcium oxide in amounts up to 2 per cent or iron oxide in amounts up to 5 per cent, are added as mineralisers.

At high temperatures, liquid is produced, the amount of which depends on the maximum temperature and the composition of the bricks. Invariably, all the alumina present enters the liquid phase and remains as a glass on cooling; associated with it are alkali and alkaline earth elements and a considerable proportion of silica, but the amount of liquid at a particular temperature in a silica brick is largely dependent on the proportion of alumina.

The crystalline phases in a fired silica refractory are usually restricted to cristobalite and tridymite. The former is the main product if lime is used as a promoter, whilst the latter is favoured by alkali elements or boiler scale which is principally iron oxide. Because the amount of calcium oxide which is required to convert raw quartzite in a reasonably short period of time is small and because, in small amounts, it does not injure the valuable properties of silica refractories, lime is the usual promoter used in the manufacture of high-grade silica bricks, which are used in furnaces to withstand temperatures of about 1650° C. Cristobalite is the only crystalline mineral formed under such conditions and because of its inversion at 220–280° C. bricks which contain it are liable to thermal shock (p. 869) if subjected to temperature fluctuations within this range of temperature. Bricks composed largely of tridymite are less liable to this defect and in all cases where silica bricks have to withstand being heated or cooled at low temperatures, tridymite bricks are preferred, e.g. in gas retorts. Because the impurity content of such bricks is relatively

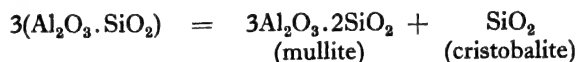
large they cannot be used at high temperatures. As stated on p. 689, commercial silica refractories frequently contain a high proportion of non-crystalline silica due to the arrested reactions in the cycle:

Quartz \rightarrow transitional phase \rightarrow cristobalite \rightarrow transitional phase \rightarrow tridymite

The proportion of non-crystalline or 'transitional phase' silica is usually higher in bricks of the greatest purity.

FIRING CHANGES IN OTHER ALUMINO-SILICATES

THE principal aluminosilicates of commercial importance apart from clays, are the kyanite, andalusite, sillimanite group which have the general formula $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$. These minerals occur in a relatively pure state in Nature and are used in the manufacture of high alumina refractories. They are stable when heated until temperatures in excess of 1000°C . are reached; above this dissociation into mullite and cristobalite occurs as shown by the following equation:



The true temperature of reaction has not been established with certainty, because the change occurs entirely in the solid state and is therefore slow. In practice the raw material is heated as high as possible to develop large crystals of mullite which confer exceptional strength on the body.

The so-called sillimanite, mullite and similar bricks are composed essentially of mullite and cristobalite with some corundum crystals united in a glassy mass. They are often made by adding an alumina-rich ore, e.g. bauxite, to a fireclay in an amount calculated to give the theoretical mullite composition.

Fused mullite articles are made by melting calcined diaspore or bauxite, grinding it to a powder, mixing it with sufficient fireclay to produce a so-called 'synthetic mullite', fusing the mixture in an electric arc furnace and casting into suitable shapes. The production is too costly for most purposes, but such bricks for glass-melting furnaces are very satisfactory. These blocks are extremely dense and resistant to erosion; they are composed of a felted mosaic of mullite needles and dendrites with glass filling voids and interstices.

Alumina bricks containing more than 92 per cent alumina contain a high proportion of corundum and some mullite. Because a clay is usually added as a bond, there is a proportion of glass, but most of the liquid formed on firing tends to crystallise on cooling as corundum or mullite.

FIRING CHANGES IN OTHER CERAMIC MATERIALS

MAGNESIA AND MAGNESITE REFRACTORIES

THE most important basic raw material for use as a refractory is magnesium oxide. It does not occur in Nature but is easily prepared by calcining the carbonate or hydroxide, both of which are available commercially (see Chapter VI). These

minerals dissociate at temperatures below 800° C. to form amorphous magnesium oxide, which, in this condition, will readily reabsorb carbon dioxide or water vapour on exposure to the atmosphere.

On being calcined at a sufficiently high temperature, magnesia slowly crystallises to *periclase* which is stable and can be cooled and maintained at room temperatures without changing form. This material which is produced by firing the magnesium mineral in a rotary kiln at about 1650° C. is known as *dead-burned magnesite*.

The formation of periclase from the amorphous oxide is a slow process even at high temperatures, but the reaction may be accelerated by the addition of certain oxides which increase the sintering rate; iron oxide is commonly employed for this purpose as also is alumina. Although such additions are necessary, they increase the proportion of impurity in the raw magnesite which in its natural state is usually contaminated with varying amounts of calcium, silicon, iron and aluminium minerals.

The total impurity content in a dead-burned magnesite, is comparatively small, yet it exerts a pronounced influence on the properties of the fired product. At high temperatures, the various components combine to form specific minerals, the nature of which is governed purely by the chemical composition. The predominant component is magnesia, and its high temperature form, periclase, may constitute 90 per cent or more of the fired product. The periclase crystals are cubic which neither intergrow or interlock and do not, as a consequence, impart strength to the material. The bonding between the periclase grains is due to the additional minerals which form through the combination of the impurities in the raw material.

The complete mineralogical composition of a fired magnesite can only be computed accurately by referring to the complex equilibrium diagram in which each component is represented. Rigby *et al*¹ have, however, evolved a simple scheme which enables the phases present in any mixture to be forecast.

The components of most magnesite materials are principally calcium oxide, magnesium oxide (in excess), iron oxide, alumina and silica in order of decreasing basicity. At the high temperatures of firing, reactions take place at a rate which depends principally on the relative affinity of the various components. Hence, the more basic components will combine most readily with those of strongest acidity, though the relative concentrations also largely determine the ultimate products. As a result of deductions made from the X-ray study of many magnesites—the chemical composition of which had been accurately assessed—Rigby, *et al*, formulated general rules for predicting the fired composition. There are two general cases.

1. When the CaO:SiO₂ molecular ratio is less than 2:1

(a) When the ratio of the *molecular concentrations* of CaO:SiO₂ is *less than 2, but greater than 1.5*. Of all the components, lime has the greatest affinity for silica, hence these two components will combine to form the stable *dicalcium silicate* 2CaO . SiO₂. The silica present in excess will combine with part of the lime and magnesia to give *merwinite* (3CaO . MgO . 2SiO₂). The relative proportions of these two minerals will depend on the CaO:SiO₂ ratio, the former predominating if this is near 2:1, but the latter becomes increasingly prevalent in mixtures where the ratio is nearer 1.5:1.

¹ Rigby, G. R., Richardson, H. M. and Ball, F., *Trans. Brit. Ceram. Soc.*, 46, 311, 1947.

(b) Where the $\text{CaO}:\text{SiO}_2$ ratio lies *between 1.5:1 and 1.0*, the silica combines with the available calcium and some magnesium. *Merwinite* is the principal phase in compositions near the higher ratio of lime:silica but *monticellite* ($\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$) also forms at lower ratios.

(c) When the ratio of $\text{CaO}:\text{SiO}_2$ is *less than 1:1* all the calcium is combined as monticellite and the excess of silica reacts with magnesia to form *forsterite* $2\text{MgO} \cdot \text{SiO}_2$.

In all cases considered above any alumina or iron oxide which may be present combines with magnesia to form *spinel* $\text{MgO} \cdot \text{Al}_2\text{O}_3$ and *magnesioferrite* $\text{MgO} \cdot \text{Fe}_2\text{O}_3$.

2. When the $\text{CaO}:\text{SiO}_2$ ratio is equal to or greater than 2:1

(a) *If the ratio is exactly 2:1*, all the lime and silica present will, theoretically, combine together to form *dicalcium silicate* and the alumina and iron oxide react with magnesia as before.

(b) *If the ratio is greater than 2:1*, all the silica combines with lime to give *dicalcium silicate*. The other phases are determined by the relative excess of lime. *Brownmillerite* ($4\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$) forms in most mixtures, although under favourable conditions *dicalcium ferrite* ($2\text{CaO} \cdot \text{Fe}_2\text{O}_3$), *tricalcium silicate* ($3\text{CaO} \cdot \text{SiO}_2$), *tricalcium aluminate* ($3\text{CaO} \cdot \text{Al}_2\text{O}_3$), or *penta-calcium trialuminate* ($5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$) and the other crystalline phases previously mentioned, may be present.

Many of these compounds have a comparatively low melting point (Table XI.X), or can form low melting point eutectics which cause the failure under stresses of magnesite refractories at comparatively low temperatures.

TABLE XI—X. MELTING OR SOFTENING POINTS OF SOME COMPOUNDS FOUND IN MAGNESITE REFRACTORIES

<i>Mineral</i>	<i>Composition</i>	<i>Melting Point °C.</i>
Periclase	MgO	2800
Forsterite	$2\text{MgO} \cdot \text{SiO}_2$	1910
Monticellite	$\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$	1500*
Merwinite	$3\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$	1575*
Dicalcium silicate	$2\text{CaO} \cdot \text{SiO}_2$	2130
Tricalcium silicate	$3\text{CaO} \cdot \text{SiO}_2$	1900
Brownmillerite	$4\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$	1415
Calcium ferrite	$\text{CaO} \cdot \text{Fe}_2\text{O}_3$	1205*
Dicalcium ferrite	$2\text{CaO} \cdot \text{Fe}_2\text{O}_3$	1436*
Tricalcium aluminate	$3\text{CaO} \cdot \text{Al}_2\text{O}_3$	1535
Pentacalcium trialuminate	$5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$	1455
Magnesioferrite	$\text{MgO} \cdot \text{Fe}_2\text{O}_3$	1751
Spinel	$\text{MgO} \cdot \text{Al}_2\text{O}_3$	2135

* Dissociates.

The **fired compositions** of many magnesite products have been calculated by Rait¹ from phase equilibria studies and confirmed by X-ray and thin-section microscopy determinations. He showed that the nature and amounts of the minerals which were present were related to the composition of the raw material. The

¹ Rait, J. R., *Basic Refractories* (Iliffe and Sons Ltd., London, 1950).

principal minerals which occur in magnesite refractories and the proportions in which they are liable to be present are summarised in Table XI.XI.

Most British magnesite refractories are made from sea-water magnesite (p. 324) and in general they contain more lime than those made from naturally-occurring carbonates. In bricks made from a material low in lime, e.g. Austrian magnesite, *monticellite* in amounts up to about 5 per cent is present. Siliceous magnesites may contain a high proportion (up to 20 per cent) of forsterite, but there is a consequent reduction in the content of periclase. The amount of glass which is found in commercial magnesites is always small in amount.

TABLE XI—XI. THE PRINCIPAL MINERALS IN
BRITISH MAGNESITE REFRACTORIES
(after Rait)

Periclase	73–88 per cent	(average 86 per cent)
Dicalcium ferrite	0–11 per cent	(average 1 per cent)
Magnesiumferrite	1–8 per cent	(average 4 per cent)
Spinel	0–7 per cent	(average 2 per cent)
Brownmillerite	0–8 per cent	(average 4 per cent)
Merwinite	0–9 per cent	(average 1 per cent)

LIME AND CALCIUM CONTAINING REFRACTORIES

CALCIUM, either as carbonate, sulphate, or aluminosilicate is a common constituent of clays where it behaves as a powerful flux or liquid-former particularly at high temperatures.

Calcium oxide either in the pure form or associated with other basic materials, such as magnesia, is a potential source of valuable refractory material. The melting point of lime is in the region of 2600° C. and the eutectic composition with magnesia does not fuse below 2200° C.

Lime does not occur in Nature but is readily produced by calcining chalk or limestone—both commonly-occurring carbonates (see p. 328)—at about 900° C. The mixed carbonate of calcium and magnesium, found as *dolomite* or *magnesian limestone* is also a common rock formation; on calcination at a high temperature, it is converted into an intimate mixture of the two oxides, lime and magnesia.

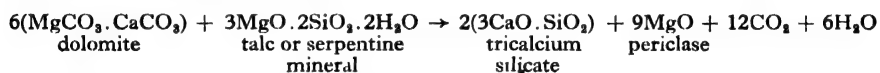
Calcium oxide, however, unlike magnesium oxide, cannot be stabilised so as to avoid atmospheric rehydration or recarbonisation merely by firing at a high temperature. Sintering may take place and the decrease of surface area thereby resulting reduces the rate of attack of water vapour or carbon dioxide, but even then deterioration and eventual disintegration proceed at a sufficient speed to prevent calcium oxide from being used as a refractory for all except small laboratory articles. Stabilisation of a temporary nature can be secured by coating the individual grains with tar to exclude air and, in this form, lime (and more particularly dolomite) is used to line basic furnaces. On calcination, however, the tar is burnt away and the lime again becomes active and would disintegrate on exposure to cold humid air.

Complete stabilisation is possible by converting the lime into a chemical compound which is not susceptible to rehydration or recarbonisation. The most obvious

choice is to form a calcium silicate, but this leads to difficulties because the ortho-variety of dicalcium silicate ($2\text{CaO} \cdot \text{SiO}_2$), (which is the one most liable to be produced by the direct combination of lime with silica), exists in three forms (see p. 113). The α - and β -varieties, which are high temperature modifications with closely similar properties, develop on calcination but, on cooling, the γ -variety forms with a large volume expansion of the order of 10 per cent. This would be sufficient to disrupt any brick or other shape which was composed of the mineral and, even when present in small amounts, dicalcium silicate causes *dusting* which is a frequent defect in dolomite bricks.

Efficient stabilisation of lime is possible by converting it into tricalcium silicate which also has inversions but these do not bring about a drastic change in property. The mineral is, however, stable only within a small range of composition (see Fig. X.50, p. 604) and any chemical additions have to be carefully controlled and blended to ensure the desired reaction.

In practice, magnesium silicate, as talc or serpentine, is normally added to the dolomite to provide silica and introduce a higher proportion of magnesia. The complete reaction is as follows:



It is considered desirable to have an excess of lime rather than silica in the fired product.

The manufacture of dolomite refractories has been considerably eased and the properties improved by stabilising α - or β -dicalcium silicate by small additions of boric oxide, chromic oxide or phosphorus pentoxide.¹ The change to γ -dicalcium silicate below 675°C . then does not occur or does so only slowly, so that the large volume expansion and consequent disruption of a shape which contains the mineral can be largely avoided.

Although bricks containing 30 per cent of stabilised α -dicalcium silicate are manufactured and do not seriously deteriorate during storage, a dolomite refractory with such a relatively high proportion would have other undesirable properties which would make it unsuitable in service. More liquid would be formed at temperatures exceeding 1600°C . and furthermore it would be less resistant to the action of slags rich in silica, lime and iron oxide, than would a brick containing chiefly tricalcium silicate. In British practice, it is usual to keep the content of dicalcium silicate below 5 per cent.²

Stabilised dolomite refractories contain a considerable proportion of impurities, similar to those in magnesite. These arise from the contaminants in the raw ores and from the additions made to promote sintering. Dolomite bricks are comparable in property to those of magnesite, but they require careful chemical control during manufacture and some have a tendency towards atmospheric deterioration.

The firing changes which take place during the burning of dolomite refractories are complex and have been studied exhaustively by Rait.³ The presence of

¹ Bates, P. H. and Klein, A. A., *Bur. Stand. Tech. Paper No. 78*, 1917.

² Swinden, T. and Chesters, J. H., *J. Iron & Steel Inst.*, **144**, 105, 1941.

³ Rait, J. R., *Basic Refractories* (Iliffe and Sons, Ltd., London, 1950).

alumina and iron oxide leads to the initial formation of a liquid at a low temperature, so that the proportion of these two impurities must be kept as low as possible. However, should alumina and iron oxide be entirely absent, liquid would not form at the usual temperatures of firing (*circa* 1450° C.) and the bricks would be of low strength. Rait has shown that the alumina and iron oxide present in a stabilised dolomite refractory usually form brownmillerite ($4\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$) and he has investigated the effects of this component on the production of liquid at high temperatures; at 1400° C., 2.0 per cent of brownmillerite produces 3.5 per cent of liquid in a mixture corresponding to periclase and tricalcium silicate; increasing the brownmillerite content to 6.0 per cent produces 8.7 per cent of liquid and with 10.0 per cent the liquid content amounts to 14.5 per cent; increasing the temperature of firing leads to the formation of more liquid. When other components, such as dicalcium silicate or spinel are present in a stabilised dolomite, the fluxing action of small amounts of brownmillerite becomes even more pronounced. From the analyses of typical dolomite refractories, Rait concluded that liquid would be formed initially at about 1280° C. and, at 1400° C., 12–16 per cent could be expected. On cooling, most of the liquid crystallises and the nature and amounts of the minerals present are shown in Table XI.XII.

TABLE XI—XII. CONSTITUTION OF
STABILISED DOLOMITE REFRACTORIES

Periclase	40–45 per cent
Tricalcium silicate	45–38 per cent
Dicalcium silicate	4–12 per cent
Brownmillerite	6–9 per cent
Spinel	1–3 per cent

Semi-stable dolomite is calcined in a rotary kiln and the lime 'stabilised' by coating the crushed, sintered mass with tar to exclude the atmosphere. A proportion of impurities is necessary to accelerate the sintering rate and to provide a flux which gives strength to the mass and to some extent 'bottles' the lime and so retards its rehydration. Free lime, periclase and a small proportion of tricalcium silicate are the principal minerals present, but amounts of brownmillerite and dicalcium ferrite which total between 5–8 per cent are invariably present.

CHROME PRODUCTS

THE essential mineral component of chrome ores is *spinel* which has the general composition $\text{R}^{2+}\text{O} \cdot \text{R}_2^{3+}\text{O}_3$ where R^{2+} is a divalent element, such as Mg and Fe^{2+} and R^{3+} is a trivalent element, for example Al, Fe^{3+} , or Cr (for more details see p. 193). Associated with this mineral are various impurities such as hydrated silicates of magnesium and iron.

On firing, the spinel grains do not change appreciably in composition, though there may be some oxidation of ferrous iron and some solid solution effects. The impurities which are more prevalent than in either raw magnesite or calcium-bearing

materials, recombine to give the typical mineral components which form the inter-crystalline linking in fired magnesites. Spinel crystals are cubic, like periclase, hence the composition of a fired chrome ore brick is similar to that of a magnesite with spinel replacing periclase and a greater predominance of crystalline impurities. Because silica is always present in appreciable amounts in chrome ores, the gangue is rich in low-melting silicates which reduce the resistance of the material to high-temperature stresses.

This drawback in chrome refractories can be largely offset by introducing finely-divided magnesia to react with the excess silica and form a proportion of forsterite which has a high melting point. Such composite materials containing 70 per cent chrome ore with 30 per cent dead-burnt magnesite are termed *chrome-magnesite* and because of their enhanced properties at high temperatures they find considerable application in steel-melting furnaces.

Chrome-magnesite refractories are composed essentially of spinel grains surrounded by a matrix which is mostly crystalline. The composition of the spinel grains depends chiefly on the constitution of the raw ore (p. 329) although some changes in the type of solid solution may occur on firing. The matrix, which comprises about 25 per cent by weight of the brick, is rich in magnesia and contains between 50–70 per cent of finely-divided periclase, forsterite is present in amounts between 12–17 per cent, whilst 10–20 per cent of monticellite ($\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$) is also to be found. The only other constituent which may occur in any quantity in the matrix is finely-divided spinel.

The behaviour of bricks under stress at high temperatures is largely dependent on the proportion of monticellite as this is a low-melting constituent which combines readily with slags rich in silica, alumina and iron. The amount of monticellite in a chrome-magnesite refractory depends on the content of lime in the raw material, hence this component should be kept as low as possible. There is, however, a limiting value because, otherwise, too little liquid would form during kiln-firing and bricks of sufficient strength could not be produced.

CHAPTER XII

PHYSICAL CHANGES IN CERAMIC MATERIALS

As with the chemical changes, it is possible to subdivide the physical changes which occur in ceramic materials during processing into (i) those which take place at ordinary temperatures (up to about 120° C.); and (ii) those which occur at elevated temperature.

CHANGES OCCURRING AT ORDINARY TEMPERATURES

In previous chapters, many of the physical changes which occur in ceramic materials have been described in detail: these include (a) changes that take place during preparation of the material (Chapter VII); (b) those which are the result of the action of water (Chapter VIII); and (c) those which accompany the loss of water or during the drying of the body (Chapter IX). This Chapter is concerned mainly with those changes which take place at elevated temperatures, but for completeness those occurring at low temperatures may be summarised.

The physical changes which take place at low temperatures in ceramic materials are chiefly concerned with:

- (a) A reduction in volume (shrinkage on drying).
- (b) Increased compactness and density.
- (c) A loss in weight (chiefly moisture but sometimes due to the evolution of a gas such as carbon dioxide).
- (d) The removal of one or more substances in solution, as in *weathering* (p. 421).
- (e) Changes in plasticity and viscosity.
- (f) Small changes also occur in the crushing strength, transverse strength, toughness, elasticity, porosity and texture, though they are much less than when a higher temperature is reached and the materials are afterwards allowed to cool.

The effects of *pressure* in increasing compactness, of *surface tension* in facilitating the moulding or extrusion of various materials, of *vapour pressure and viscosity* in connection with the extrusion of clay bodies, of *flocculation and deflocculation*, all require much attention in various researches as well as in industrial production.

At 'low' temperatures many of these reactions and other changes cannot proceed to completion, though various degrees of stability may be reached and they are of considerable technical importance. Thus the appearance and behaviour of a piece of highly plastic clay are very different from the same piece after it has been allowed to dry at ordinary room temperature and slightly more so after more complete drying at 105°–110° C. Hence the importance of considering such changes as occur at 'low' temperatures apart from those which occur at higher ones.

These physical changes are practically the same as those which occur both at

ordinary room temperatures and at any temperature up to 120° C. (though in some cases some decomposition also occurs as the temperature of 100°–120° C. is reached), but the changes usually associated with drying are accelerated by the application of gentle heat or by a current of warmed air.

PHYSICAL CHANGES WHICH OCCUR IN CERAMIC MATERIALS AT ELEVATED TEMPERATURES

IN the previous chapter, the chemical changes which occur on heating ceramic materials have been considered. Firing treatment also causes a pronounced alteration in the purely physical and textural properties either as the direct consequence of a change in the physical properties of the minerals present (e.g. expansion, specific gravity) or through chemical action (e.g. liquid formation, crystalline development).

It is not possible or even desirable to distinguish between the two types of effects in many cases, but their combined action may be observed in the various changes which take place in the textural properties of the body as follows:

- (a) A change in the temperature of the mass.
- (b) A change in state of the material, i.e. from a solid to a liquid or to a gas.
- (c) A change in the volume of the material (expansion or contraction).
- (d) A change in the porosity of the body.
- (e) A change in the specific gravity of the material.
- (f) A change in the strength of the body.
- (g) A change in weight in the mass.
- (h) Changes in other physical properties, e.g. optical, electrical, thermal, feel, hardness, etc.
- (i) A change in colour.

CHANGES IN TEMPERATURE

CHANGES in temperature may be purely physical in character and a simple result of what is termed the absorption of heat (this may simultaneously effect a change in the physical state of the substance, p. 701), or they may be the result of chemical changes which evolve or absorb heat.

The rate and manner in which a mass will increase in temperature depends on several factors, the most important of which are outlined below:

(i) The *difference between the temperature of the environment and that of the body itself*. Heat, being a form of energy, is readily transferred from a hot to a cold source at a rate proportional to the temperature difference.

(ii) The *total heat content of the source*. A hot object behaves as a reservoir of heat; if it is small in size or of a low heat capacity (see p. 846) it will not have much heat to impart to a cold body with which it comes into contact. On the other hand, if a body is placed into a furnace of large heat capacity, it will be quickly raised in temperature without appreciably altering the environmental conditions.

(iii) The *mechanism of heat transfer to the cold body*. A solid body can receive heat either by conduction or radiation. The former process requires that the source

of heat be in direct contact and the transfer of energy is from particle to particle of the materials involved. *Conduction* will take place when a cold body touches another at a higher temperature or equally when hot gases are circulated round the mass. Although other factors are involved, the rate of conduction is directly proportional to the difference in temperature.

Radiation is of an entirely different nature. Heat is similar to light in that it can be transmitted in the form of energy waves of a certain frequency; these rays are of longer wavelength than those of the visible part of the spectrum but their mode of transmission is identical. Heat is therefore radiated from a hot body and can be absorbed within a suitable receptive material which is raised in temperature as a consequence, but the intervening medium, usually air or gas which transmits the rays is little changed in temperature. The amount of heat absorption depends on the nature of the material and also its surface, but it is approximately proportional to the difference between the fourth powers of the temperature of the source and receptive materials, i.e. to $T_s^4 - T_o^4$, where T_s is the temperature of the source of radiating heat and T_o is the temperature of the body being heated.

(iv) The *surface of the body* exposed to the source of heat and the *geometrical shape*. The heating of a shape by an external agency proceeds from the surface exposed through the mass of material. It is an obvious fact that a brick will more readily reach a uniform temperature throughout if it is heated on all sides than if only one or two faces were exposed. Similarly, a small specimen will heat up more quickly than one of larger size under the same conditions.

(v) The *specific heat of the material* being heated. Different substances have varying capacities for absorbing heat, some needing far more heat to raise a unit weight to a given temperature than do others (see Chapter XIV).

(vi) The *thermal diffusivity* of the body or the rate at which heat is transmitted through the material. In ceramic bodies which may be regarded as porous aggregates, heat transfer is a highly complex phenomenon and will be considered in detail in Chapter XIV.

(vii) *Exothermal or endothermal changes* within the material being heated. As the temperature of a substance is raised, reactions of a chemical or physical nature may occur which are accompanied by either an absorption or liberation of heat. The former are known as endothermal and the latter as exothermal changes. In addition to purely chemical reactions involving decomposition or recombination, changes of state from solid to liquid or liquid to gas may be accompanied by thermal effects which alter the rate of heating of a substance at a particular temperature. When ceramic clay materials are fired in the kiln, a temperature arrest frequently occurs on the decomposition of the clay minerals; alternatively, if carbonaceous constituents are present, the heat liberated during oxidation may increase the rate of temperature rise to an alarming degree.

CHANGES OF STATE

AN important influence of heat on ceramic materials is the change from a solid to a liquid form. The formation of a liquid is a true physical effect, but in materials of a complex composition, liquefaction is often accompanied by a chemical change.

The factors which influence the melting point of simple compounds have been described in Chapter X, but only if a material is very pure and of a simple structure will it melt at a definite temperature. Even when a substance is almost pure, the change of state proceeds at a rate which depends on the smallness of the individual particles and if the liquid formed is viscous, the melting of a large volume does not proceed readily.

Ceramic materials are seldom pure and for this and many other reasons (p. 641) they do not have a definite melting point. It is customary to refer to the *softening point* of a ceramic material which is the temperature at which it first shows visible signs of fusion, such as the rounding of the sharp edges of the test piece. The softening point is often defined as the temperature at which the sample commences to deform under an applied force (see Refractoriness-under-load, p. 775).

The Refractoriness of Ceramic Materials. For practical purposes the fusibility or resistance to heat of a ceramic material is generally defined in terms of *Refractoriness* which is the temperature at which a test sample of specified shape and size is deformed a specific amount under particular heating conditions. It is customary to measure the refractoriness of a material¹ by either moulding a powdered sample or cutting a piece from a block into a cone, the base of which is an equilateral triangle of 1.5 cm. side and the height of which is 5 cm. One vertical edge of the cone is at right angles to the base so that the centre of gravity is displaced to one side and when fusion commences, the tip of the cone bends in a predetermined direction. The refractoriness of a specimen is defined as the temperature at which the tip of the test cone just touches the base on which the cone rests when it is heated at 10° C. per minute.

Because it is difficult to measure the precise moment at which the cone has deformed the correct amount, accurate measurements of the refractoriness are usually made by comparing the behaviour of a test specimen with standard cones of which those devised by Seger are most commonly employed in this country. Seger cones are made of artificial mixtures similar to porcelains; their composition is adjusted so that they bend at a specific temperature under a controlled rate of rise. In Table XII.IA, the composition and melting points of a series of cones are illustrated;

TABLE XII—I A. COMPOSITION OF SEGER CONES

Potash	Soda	Lime	Lead Oxide	Alu- mina	Iron Oxide	Silica	Boric Oxide	Cone No.	Estimated Tempera- ture, ° C.
—	0.5	—	0.5	—	—	2	1	022	600
—	0.5	—	0.5	0.1	—	2.2	1	021	650
—	0.5	—	0.5	0.2	—	2.4	1	020	670
—	0.5	—	0.5	0.3	—	2.6	1	019	690
—	0.5	—	0.5	0.4	—	2.8	1	018	710
—	0.5	—	0.5	0.5	—	3	1	017	730
—	0.5	—	0.5	0.55	—	3	1	016	750
—	0.5	—	0.5	0.6	—	3.2	1	015	790
—	0.5	—	0.5	0.65	—	3.3	1	014	815
—	0.5	—	0.5	0.7	—	3.4	1	013	835
—	0.5	—	0.5	0.75	—	3.5	1	012	855

¹ British Standards Institute (London, 1952) and ASTM Designation C24-46, 1946.

TABLE XII—IA. COMPOSITION OF SEGER CONES—*continued*

Potash	Soda	Lime	Lead Oxide	Alu- mina	Iron Oxide	Silica	Boric Oxide	Cone No.	Estimated Tempera- ture, ° C.
—	0.5	—	0.5	0.8	—	3.6	1	011	880
0.3	—	0.7	—	0.3	0.2	3.50	0.45	010	900
0.3	—	0.7	—	0.3	0.2	3.55	0.50	09	920
0.3	—	0.7	—	0.3	0.2	3.60	0.40	08	940
0.3	—	0.7	—	0.3	0.2	3.65	0.35	07	960
0.3	—	0.7	—	0.3	0.2	3.70	0.30	06	980
0.3	—	0.7	—	0.3	0.2	3.75	0.25	05	1000
0.3	—	0.7	—	0.3	0.2	3.80	0.20	04	1020
0.3	—	0.7	—	0.3	0.2	3.85	0.15	03	1040
0.3	—	0.7	—	0.3	0.2	3.90	0.10	02	1060
0.3	—	0.7	—	0.3	0.2	3.95	0.05	01	1080
0.3	—	0.7	—	0.3	0.2	4	—	1(a)	1100
0.3	—	0.7	—	0.4	0.1	4	—	2(a)	1120
0.3	—	0.7	—	0.45	0.05	4	—	3(a)	1140
0.3	—	0.7	—	0.5	—	4	—	4(a)	1160
0.3	—	0.7	—	0.5	—	5	—	5(a)	1180
0.3	—	0.7	—	0.6	—	6	—	6(a)	1200
0.3	—	0.7	—	0.7	—	7	—	7	1230
0.3	—	0.7	—	0.8	—	8	—	8	1250
0.3	—	0.7	—	0.9	—	9	—	9	1280
0.3	—	0.7	—	1.0	—	10	—	10	1300
0.3	—	0.7	—	1.2	—	12	—	11	1320
0.3	—	0.7	—	1.4	—	14	—	12	1350
0.3	—	0.7	—	1.6	—	16	—	13	1380
0.3	—	0.7	—	1.8	—	18	—	14	1410
0.3	—	0.7	—	2.1	—	21	—	15	1435
0.3	—	0.7	—	2.4	—	24	—	16	1460
0.3	—	0.7	—	2.7	—	27	—	17	1480
0.3	—	0.7	—	3.1	—	31	—	18	1500
0.3	—	0.7	—	3.5	—	35	—	19	1520
0.3	—	0.7	—	3.9	—	39	—	20	1530
0.3	—	0.7	—	4.4	—	44	—	21	Not manu- factured
0.3	—	0.7	—	4.9	—	49	—	22	
0.3	—	0.7	—	5.4	—	54	—	23	
0.3	—	0.7	—	6.0	—	60	—	24	
0.3	—	0.7	—	6.6	—	66	—	25	
0.3	—	0.7	—	7.2	—	72	—	26	1580
0.3	—	0.7	—	20.0	—	20.0	—	27	1610
—	—	—	—	1	—	10	—	28	1630
—	—	—	—	1	—	8	—	29	1650
—	—	—	—	1	—	6	—	30	1670
—	—	—	—	1	—	5	—	31	1690
—	—	—	—	1	—	4	—	32	1710
—	—	—	—	1	—	3	—	33	1730
—	—	—	—	1	—	2.5	—	34	1750
—	—	—	—	1	—	2	—	35*	1770
—	—	—	—	1	—	2	—	36†	1790
—	—	—	—	1	—	1.66	—	37	1825
—	—	—	—	1	—	1.33	—	38	1850
—	—	—	—	1	—	1	—	39	1880
—	—	—	—	1	—	0.66	—	40	1920
—	—	—	—	1	—	0.33	—	41	1960
—	—	—	—	1	—	—	—	42	2000

* Kaolin.

† Clay schist.

different manufacturers have modified the composition of the cones slightly but the code number and the temperature at which bending occurs are applicable to all Seger cones provided that the rate of rise of temperature is maintained at 10° C. per minute. In the U.S.A., Orton cones are in more general use; whilst they are similar in composition to Seger cones and the temperature of fusion of a particular cone is not very different, they are designed to be used at a much smaller rate of temperature rise as shown in Table XII.In.

TABLE XII—In. CHARACTERISTICS OF ORTON CONES*

Cone No.	Bending Temperature		Cone No.	Bending Temperature		Cone No.	Bending Temperature	
	° C.	° F.		° C.	° F.		° C.	° F.
1	1160	2120	14	1400	2552	27	1605	2921
2	1165	2129	15	1435	2615	28	1615	2939
3	1170	2138	16	1465	2669	29	1640	2984
4	1190	2174	17	1475	2687	30	1650	3002
5	1205	2201	18	1490	2714	31	1680	3056
6	1230	2246	19	1520	2768	32	1700	3092
7	1250	2282	20	1530	2786	32½	1722	3131
8	1260	2300	21	—	—	33	1745	3173
9	1285	2345	22	—	—	34	1760	3200
10	1305	2381	23	1580	2876	35	1785	3245
11	1325	2417	24	—	—	36	1810	3290
12	1335	2435	25	—	—	37	1820	3308
13	1350	2462	26	1595	2903	38	1835	3335

* Heating rate: Cones Nos. 1–20, 150° C. per hour.
Cones Nos. 23–38, 100° C. per hour.

The refractoriness of a sample is measured by cementing a cone of the material on a suitable base along with a range of standard cones. The approximate refractoriness of the substance under test should be determined beforehand so that not more than five standard cones need to be used. The assembly is mounted in a furnace and the temperature raised at 10° C. per min. until the sample cone begins to deform. The cone carrier is then removed from the furnace and the deformation of the test sample compared with those of the standard cones; the number of the cone which it most closely resembles is taken as the refractoriness.

Many factors other than composition affect the refractoriness of a sample. The state of subdivision is one of the most important considerations and when testing a raw material, e.g. clay, a standard method of preparing the sample should be adopted and the clay ground to pass a 100 B.S.S. The refractoriness of a fired body is best carried out on a cone cut directly from a block of the material. When the test sample contains iron compounds, an oxidising atmosphere must be maintained in the furnace throughout the test, otherwise, low-melting ferrous compounds will form and give rise to a low refractoriness. The refractoriness of bloating clays is particularly difficult to measure, because the test cone is seriously distorted at high temperatures; a satisfactory test is sometimes possible if the sample is precalcined at about 1200° C.

Chemical Composition and Refractoriness. Many attempts have been made to find a definite relationship between the composition of clays and their refractoriness.

So far it has been impossible to find any definite rule which can be applied to all clays, but with the purer clays, such as fireclays and kaolins, where there are fewer factors to be considered, a rough relationship has been found to exist. No exact correlation is possible, because the refractoriness depends on the size of the particles and on their contact as well as on the composition of the material.

Several formulae have been suggested which are satisfactory within narrow ranges of composition, but the most suitable method which is surprisingly accurate within much wider limits is due to Ludwig, who compiled a chart from which the refractoriness of a clay may be calculated. Ludwig based his chart on the assumption that clays, when fired, form solid solutions of the minerals constituting the 'impurities'

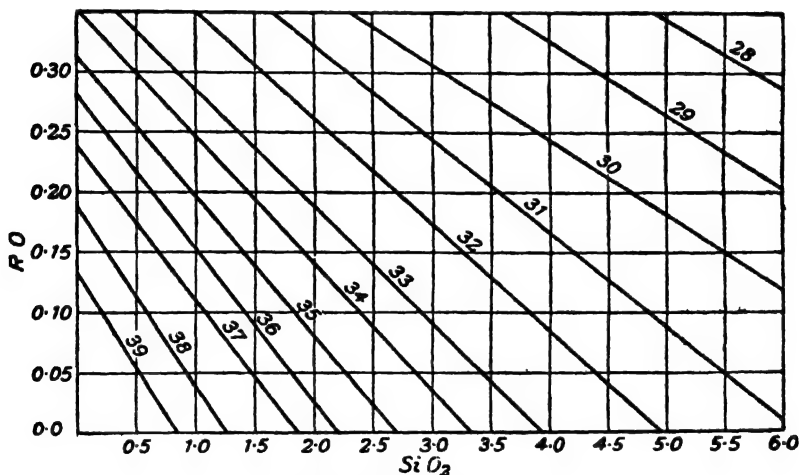


FIG. XII.1. LUDWIG'S CHART

in the clay and that they must, therefore, reduce the melting point of the clay in proportion to their molecular concentration. He determined the refractoriness of many clays of different compositions and then calculated their formulae, assuming the alumina to be unity, i.e. $x(R_2O + RO) \cdot Al_2O_3 \cdot ySiO_2$. He then marked off the refractoriness of the clays on a graph having the molecular ratios of $R_2O + RO$ as ordinates and those of SiO_2 as abscissae. Iron oxide should be calculated as FeO . When the iso-refractory lines corresponding to the various Seger cones are plotted on the graph, they enable the refractoriness of any material of a composition lying on or between any of these lines to be ascertained with a fair degree of accuracy. This chart is very useful for clays containing up to 6 per cent of bases, but for less pure clays it is useless, on account of the heterogeneous nature of the materials. Ludwig's chart is shown in Fig. XII.1.

Although the presence of impurities greatly increases the fusibility of clays, it is a surprising fact that the refractoriness of aluminosilicates is very largely a property of the ratio of their alumina to silica contents. Mellor and Green¹ have shown that

¹ Mellor, J. W. and Green, A. T., *J. Soc. Chem. Ind.*, 57, 627, 1938.

different manufacturers have modified the composition of the cones slightly but the code number and the temperature at which bending occurs are applicable to all Seger cones provided that the rate of rise of temperature is maintained at 10° C. per minute. In the U.S.A., Orton cones are in more general use; whilst they are similar in composition to Seger cones and the temperature of fusion of a particular cone is not very different, they are designed to be used at a much smaller rate of temperature rise as shown in Table XII.B.

TABLE XII—B. CHARACTERISTICS OF ORTON CONES*

Cone No.	Bending Temperature		Cone No.	Bending Temperature		Cone No.	Bending Temperature	
	° C.	° F.		° C.	° F.		° C.	° F.
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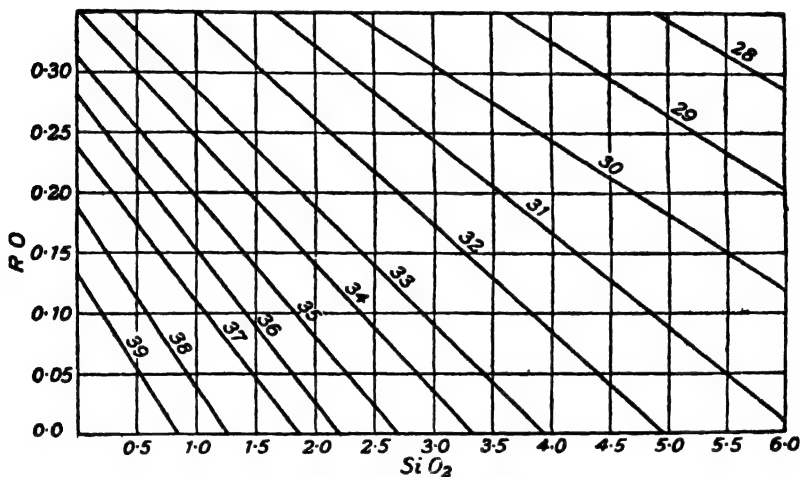


FIG. XII.1. LUDWIG'S CHART

in the clay and that they must, therefore, reduce the melting point of the clay in proportion to their molecular concentration. He determined the refractoriness of many clays of different compositions and then calculated their formulae, assuming the alumina to be unity, i.e. $x(R_2O + RO) \cdot Al_2O_3 \cdot ySiO_2$. He then marked off the refractoriness of the clays on a graph having the molecular ratios of $R_2O + RO$ as ordinates and those of SiO_2 as abscissae. Iron oxide should be calculated as FeO . When the iso-refractory lines corresponding to the various Seger cones are plotted on the graph, they enable the refractoriness of any material of a composition lying on or between any of these lines to be ascertained with a fair degree of accuracy. This chart is very useful for clays containing up to 6 per cent of bases, but for less pure clays it is useless, on account of the heterogeneous nature of the materials. Ludwig's chart is shown in Fig. XII.1.

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the refractoriness of commercial alumino-silicate refractories bears a similar relationship to the equilibrium diagram of pure alumina and silica except that the temperatures are not directly comparable (Fig. XII.2). The refractoriness of many fireclays can be implied from the ratio of their contents of alumina and silica.

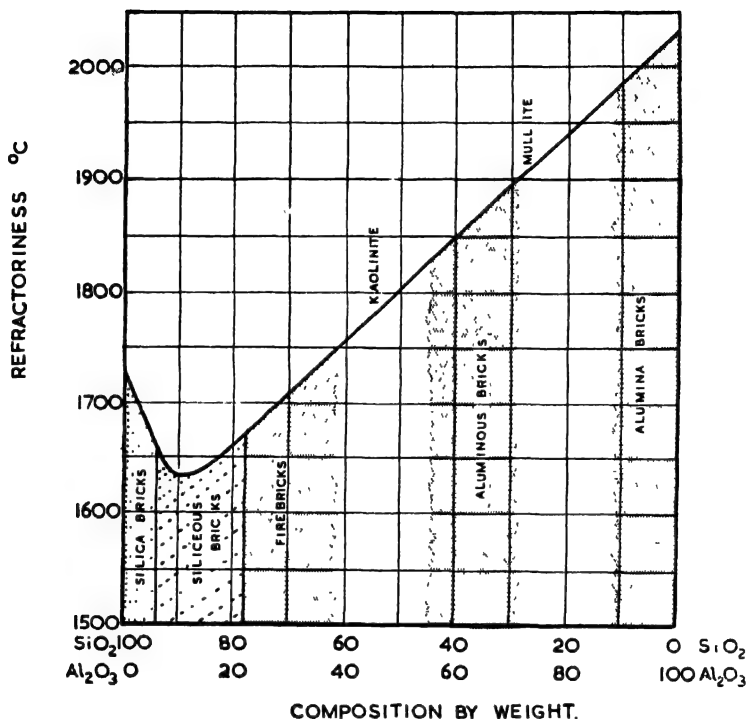


FIG. XII.2. THE REFRACTORINESS OF COMMERCIAL ALUMINO-SILICATE MATERIALS
(after Mellor and Green)

Building Bricks are not very refractory because of their high content of fluxes. Their fusion point is usually in the range 1250°–1350° C. but many of them bloat excessively below this temperature.

Fireclay bricks vary greatly in refractoriness, according to the raw material of which they are made. Such bricks are not generally regarded as 'refractory' if they have a heat-resistance of less than that of Cone 26 when tested as described on p. 702. The best fireclays have a refractoriness of about Cone 34 (1750° C.), but most first-class fireclay bricks average Cone 31–32 with a minimum of Cone 30, whilst the second-class bricks may have as low a refractoriness as Cone 26. Bricks with a still lower refractoriness should only be employed for purposes where they are not exposed to great heat, so that a high refractoriness is not required.

First-class firebricks must have a refractoriness greater than Cone 30 and second-class bricks must not be less than Cone 26.

The American Society for Testing Materials specifies the following refractory requirements for fireclays and aluminous bricks.¹

	<i>Minimum Orton Cone Number</i>
70 per cent alumina-diaspore brick	36
60 per cent alumina-diaspore brick	35
50 per cent alumina-diaspore brick	34
Super duty fireclay brick	33
High duty fireclay brick	31-32
Intermediate duty fireclay	29
Low duty fireclay brick	19

A British specification is shown in Table XII.XII, p. 730.

Fireclay mortars and cements should have as high a refractoriness as possible, but because they frequently contain additives to increase their plasticity and strength they are usually less resistant to heat than bricks.

Some *refractory porcelain* has a refractoriness of Cone 30-31 (1680° C.) but the glaze begins to soften at a much lower temperature.

The best quality **silica bricks** have a refractoriness from Cone 34 to Cone 36 (1750°-1790° C.) which is greater than the melting point of pure silica; molten silica is highly viscous and does not flow readily, hence the deformation of cones rich in silica is at a very slow rate. Low grade silica bricks may have a refractoriness not greater than Cones 31-33 and semi-silica bricks do not usually exceed Cone 26.

Fused silica, when tested as described on p. 702, has a refractoriness of 1700°-1800° C., but if heated under pressure or in the form of a long bar or rod supported only at its ends, it may soften sufficiently to lose its shape at 1500° C. Articles made of fused silica should not usually be subjected to prolonged heating at temperatures above 1200° C. (see p. 748).

Silica mortar or cement should have a refractoriness as nearly as possible equal to that of the bricks with which it is to be used, the difference between them not being greater than 100° C. (five cones). The Institution of Gas Engineers has specified that the cement shall be quite suitable for the purpose of binding the bricks for which it is supplied and shall be capable of withstanding the same test for refractoriness.

Bauxite bricks are very refractory; when the bauxite is almost pure, the softening point is between Cones 36 and 39 (1790°-1880° C.). As the refractoriness of bauxite bricks increases, their strength decreases, so that the strongest bricks are those which contain 20 per cent or more of silica and a refractoriness corresponding to Cones 33-35 (1730°-1770° C.), which is little, if any, higher than that of silica bricks.

Magnesite and dolomite bricks made of the purest materials with a minimum bond are very refractory and do not soften below Cone 40 (1920° C.), but in order to produce bricks of sufficiently great strength a large proportion of bond is usually employed, and this—being in the nature of a flux—reduces the refractoriness of the bricks.

¹ A.S.T.M., Designation C.27-41, 1941.

Carbon bricks are the most refractory materials used in furnace construction, as they do not soften at any temperature reached in industry. They have the disadvantage, however, of slowly burning away if exposed to oxidising conditions, and they are very weak both as regards mechanical strength and in their resistance to abrasion.

Silicon carbide bricks are more refractory than fireclay, silica, and magnesite bricks, but they cannot be maintained at high temperatures for a long period on account of their decomposition, which commences at temperatures over 2000° C. in the absence of air and at about 1400° C. in an oxidising atmosphere. For this reason, their use at very high temperatures is limited.

TABLE XII—II. MELTING POINTS OF CERAMIC MATERIALS

<i>Mineral</i>	<i>Melting point or Range, ° C.</i>	<i>Mineral</i>	<i>Melting point or Range, ° C.</i>
Alumina	2049	Lime (pure)	2570
"	1880	Magnesia	2800
"	2020	"	2250
"	2050	"	1910
Barium oxide	1925	"	2000
Bauxite	1820	"	2050-2100
"	1600-1800	"	2150
Bauxite brick	1565-1785	Magnesite brick	2165
Bauxitic clay	1795	Molybdenum carbide	2700
"	1800	Quartz	1710
Beryllium oxide	2525	Silica brick	1700-1750
Boron carbide	2400	Silica sand	1700-1750
Cerium oxide	2950	Silicon carbide	2700
Chromite	2180	Sillimanite	1800
Chromite brick	2050	Tantalum pentoxide	1875
Chromium oxide	1990	Thoria	2470
"	2059	Titanium oxide (rutile)	1600-1700
Corundum	1950	Tungsten carbide	3000
Dolomite	2100	Yttria	2400
Fireclay brick	1555-1725	Zircon	2550
Kaolin	1735-1740	Zirconia	2590
Lanthanum oxide	1840	Zirconium carbide	3200

Saggars and muffles vary in refractoriness according to the purpose for which they are to be used. Simple refractoriness is not sufficient, as these articles must not lose their shape under load at any temperature likely to be reached when they are in use. Saggars or muffles for burning hard porcelain must have a refractoriness at least equal to that of Cone 35; for bone china, a refractoriness equal to Cone 30 (1670° C.) is sufficient, whilst for inferior ware still less refractory saggars or muffles may be employed. In judging saggars, it is preferable to consider refractoriness under load (p. 775) rather than simple refractoriness, as the loads which saggars often support in a kiln are somewhat stringent.

Glass-melting pots should have a high refractoriness as the conditions under which they are used are very stringent. They should be as refractory as the best quality of material used for firebricks, especially under load.

Table XII.II compiled from the results of various investigators, shows the melting points of various ceramic materials.

TABLE XII—III. MELTING POINTS OF MINERALS

<i>Mineral</i>	<i>Melting-point or Range, ° C.</i>	<i>Mineral</i>	<i>Melting-point or Range, ° C.</i>
Albite	1120–1220	Galena	1115
Alumina	2050	Gehlenite	1570
Andalusite	1770	Grossular	1150–1250
Anorthite	1532	Hornblende	1180–1220
Apatite	1270–1300	Kaolin	1745–1790
Asbestos	1285–1310	Labradorite	1477
Augite	1145–1150	Lepidolite	925–945
Barium metasilicate	1490	Leucite	1320–1370
Barium metaborate	1050	Magnesia	2500
Barium orthoborate	1350	Magnesium metasilicate	1565
Barium pyroborate	1000	Magnesium orthosilicate	1900
Bauxite	1820	Magnetite	1538
Beryl	1410–1430	Monticellite	1435
Beryllium metasilicate	2000	Mullite	1810
Beryllium orthosilicate	2000	Muscovite	1255–1290
Biotite	1155–1240	Nepheline	1223
Borax	878	Nephite	1180–1210
Bronzite	1310–1370	Olivine	Over 1600
Calcium aluminate	1587	Orthoclase	1175–1225
Calcium diborate	1025	Potassium metaborate	947
Calcium metaborate	1095	Rhodonite	1210
Calcium pyroborate	1215	Rutile	1700
Calcium phosphate	1550	Scapolite	1120–1140
Calcium orthosilicate (α)	2130	Silica (quartz)	1685*
Calcium metasilicate (α)	1540	Sillimanite	1816
Tricalcium aluminate	1537	Sodium chloride	819
Tricalcium ferrite	1455	Sodium metaborate	960
Chromite	1850–2180	Sodium metasilicate	1018
Corundum	1750–1800	Spinel	2135
Cristobalite	1720	Spodumene	1380
Cryolite	977	Strontium metasilicate	1287
Diopside	1391	Strontium orthosilicate	1593
Enstatite	1380–1500	Titanite	1200–1300
Epidote	1250	Titanium oxide	1610
Fayalite	1210	Titanium orthosilicate	1650
Ferrous oxide	1419	Tourmaline	1000–1100
Ferrous metasilicate	1100	Wollastonite	1540
Ferric oxide	1548	Zinc metasilicate	1479
Fluorite	1361	Zinc orthosilicate	1484
Forsterite	1910		

* α -Quartz is inverted at 573° C. to β -Quartz, which, if finely ground, is converted at 870° C. into tridymite, and at 1470° C. into cristobalite; the last-named melts at 1720° C.

The melting points of the various minerals likely to occur in ceramic materials are shown in Table XII.III, compiled from the results of various investigators.

The change of ceramic materials into vapours is seldom regarded as a simple physical change. It is usually one result of chemical decomposition such as the reduction of silica to silicon monoxide or silicon which are readily volatilised at high temperatures, but are soon re-oxidised and deposited as a white powder. This may appear as though silica itself is volatilised in some furnaces but that is not the case.

The melting of some components in a ceramic material alters many of the physical characteristics of the substance. It may cause a change in the size or shape

and, on cooling, articles in which large amounts of liquid have been present will be much changed in texture and surface appearance. They will be vitrified (p. 673), and may have altered drastically in colour.

CHANGES IN VOLUME

CHANGES in volume effected by heat result in either an increase or a decrease in the volume of the substance; the former is termed *expansion* and the latter *contraction* or *shrinkage*. These changes are often of great technical importance, especially when substances which undergo such changes are made into articles which are required to be of definite size within very narrow limits. Thus, first-class firebricks are not expected to vary in length by more than 1 per cent, whilst for some electrical fittings made of stoneware or porcelain a much greater degree of accuracy in size is required.

The changes in volume caused by the action of heat may be divided into two groups: (a) reversible, and (b) irreversible changes.

(a) *Reversible volume-changes* are those in which the volume of a substance changes on the application of heat, but the original volume is regained when the heat is withdrawn, i.e. when the substance is cooled to the original temperature. Such changes are usually of a wholly physical nature.

(b) *Irreversible changes* are those in which any increase or decrease in volume which may occur is permanent and is not reversed on cooling. Such a change may be the result of the formation of a substance of different specific gravity, such as the conversion of quartz to cristobalite, or some change of a chemical character whereby new compounds are formed.

A change of state which results in the formation of a liquid phase may give rise to an irreversible shrinkage of the mass especially if the initial porosity were high.

REVERSIBLE CHANGES ON HEATING

The *reversible changes on heating* are of two kinds: (i) the normal coefficient of expansion or contraction associated with all materials; and (ii) sudden volume changes accompanying reversible reactions, e.g. the $\alpha \rightleftharpoons \beta$ inversion of quartz.

The coefficient of expansion or contraction is expressed as a fraction of the length, cross-sectional area, or volume of the substance (the latter being taken as unity) when heated so that its temperature rises 1°C. , though any suitable temperature may be used, provided it is specified. The coefficient of expansion may be expressed in terms of length, i.e. the coefficient of linear expansion, or in terms of volume, i.e. the coefficient of cubical expansion. If the coefficient of linear expansion is represented by a , the original length of the piece being l_0 at 0°C. and l_t at $t^\circ \text{C.}$, then

$$l_t = l_0(1 + at)$$

Hence, if the length prior to expansion be unity, that after expansion will be $(1 + a)$ and the volume after expansion will be $(1 + a)^3$ or $1 + 3a + 3a^2 + a^3$. As a is a small fraction, a^2 and a^3 will often be so small as to be negligible, and it is then

sufficient to regard the volume of the expanded material as $(1 + 3a)$. Hence, the coefficient of volume expansion is almost exactly three times the linear coefficient. If the linear expansion or contraction is as high as 10 per cent, omitting the fractions as suggested will produce an error of about 10 per cent of the total volume change.

Most pure substances expand suddenly when melted, but a few (notably ice and bismuth) contract. Thus, 1000 cc. of ice yield only 910 cc. of water at 0° C. This expansion or contraction relates to the individual particles and not to the mass as a whole, as in a porous material the air spaces may be filled by the molten material.

The expansion of materials on heating may be determined in various ways. Where it is large, as in the case of some metals, a bar is heated with one end fixed and the other in contact with an indicating lever and the amount of deflection noted.

The standard method now in common use for ceramic materials is to heat a square-ended or cylindrical specimen in a silica glass sheath, which, in turn, fits loosely into a tubular wire-wound furnace. The specimen is supported on a silica rod and a distance rod of the same material rests on top of the test bar and projects out of the fused silica sheath which is maintained in a vertical position. The complete assembly is shown in Fig. XII.3, including the dial gauge which is attached to the silica sheath. Its pointer is in contact with the end of the protruding distance piece, hence the relative difference in expansion between the internal assembly and the outside sheath can be accurately measured.

The expansion of the bar under test can be calculated relatively simply from such an apparatus.

If the silica sheath is l cms. in length and the specimen is x cms. long, the expansion recorded on the dial gauge at any particular temperature t is the increase in length of the specimen (of x cms.) plus the expansion of the internal, silica supporting rod and distance piece (of equivalent length $l-x$ cms.) minus the expansion of the outside silica sheath (of length l cms.).¹

If the coefficient of expansion of silica is α_1 and that of the test specimen α_2 , the dial gauge reading may be expressed as:

$$\begin{aligned}\text{Reading} &= (x\alpha_2 + (l-x)\alpha_1 - l\alpha_1)t \\ &= (x\alpha_2 - x\alpha_1)t\end{aligned}$$

The expansion of the specimen itself, i.e. $x\alpha_2 t$, is thus the reading on the dial gauge plus the expansion of an equivalent length of a fused silica rod. This latter is relatively small and can be calculated by using a material of known expansion characteristics or from data supplied by the makers.

In practice, the expansion test is best carried out using an extremely small rate of temperature rise (about 1° C. per minute should not be exceeded).

Fused silica rods and sheaths are serviceable only for measurements up to 1000° C.; above this temperature mullite should be substituted and, as this material has a much larger expansion than silica, greater care must be taken with the initial calibration.

¹ As the dial gauge is supported by the sheath any increase in length in the latter would be indicated as a contraction reading, hence it would have to be subtracted from the overall indication on the gauge.

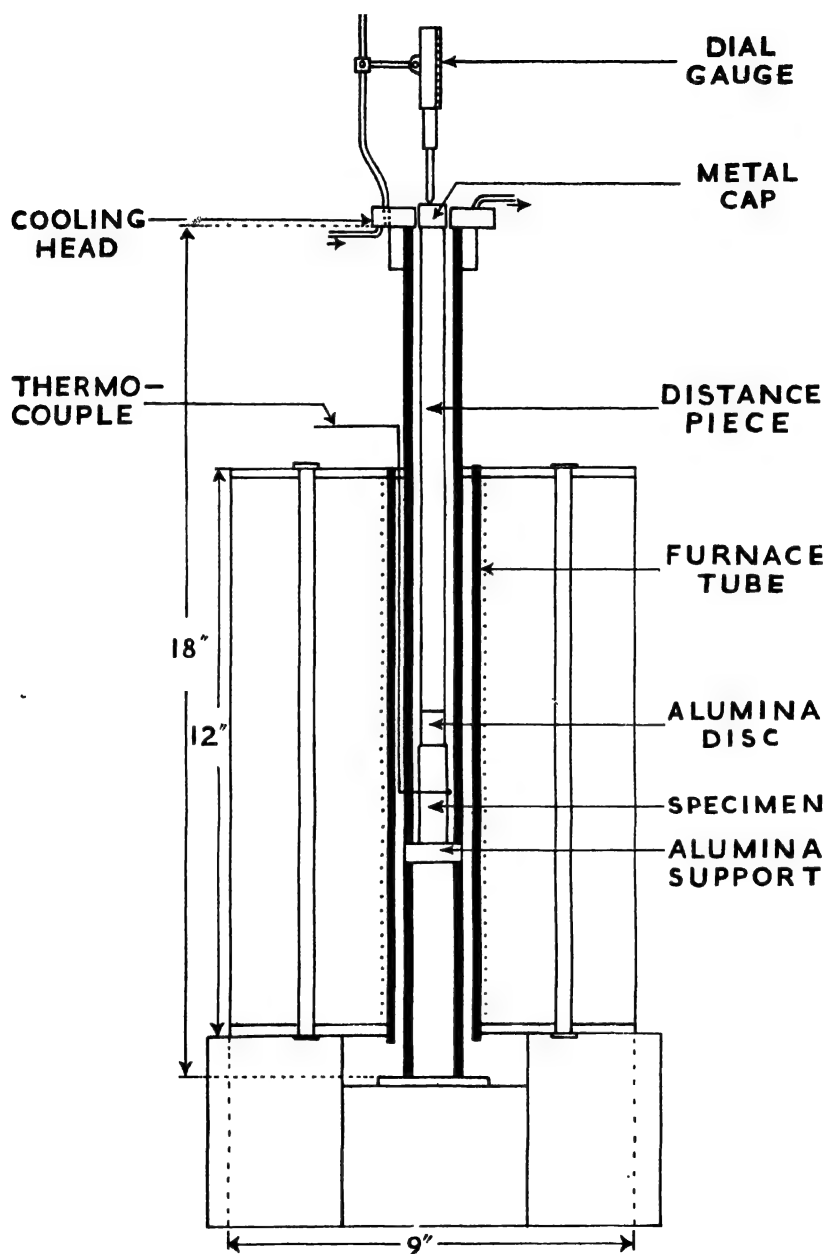


FIG. XII.3. AN APPARATUS FOR MEASURING THE THERMAL EXPANSION OF CERAMIC MATERIALS

In recent years, similar equipment has been described for measuring the expansion of small-sized specimens. The dial gauge is then usually replaced by a more sensitive indicating or recording device. An optical lever arrangement has been used by some workers; others prefer to make the top of the distance piece one plate of a condenser with the other fixed and the whole forming part of an electrical circuit. Both these methods enable a continuous record of the expansion curve to be made.

By such means, the linear change in size of a material may be measured and hence its coefficient of expansion or contraction. In addition, any inflection in the curve may be detected and related to inversional changes and associated phenomena in the minerals present.

Reversible Volume Changes on heating occur to a greater or less extent in all materials. Basically, they are the result of changes within the crystalline lattices of the component minerals due to the heating effect, and on cooling the body returns to its former size. Reversible volume changes depend on the coefficient of expansion (or contraction) of the body, and this varies with different materials according to

- (a) the mineralogical composition;
- (b) the texture.

The coefficient of expansion of minerals. Numerous recent attempts to correlate the thermal expansion properties of materials with their crystalline structure have met with a considerable amount of success with simple crystals, but more complex substances—particularly some of those of interest to the ceramist—are still beyond the scope of theoretical treatment.

The present-day concept of matter has been outlined in Chapter II. Crystals are considered to be composed of atoms or ions, arranged in particular geometrical patterns and forming crystalline lattices. Although it is convenient to regard each unit of such a lattice as having a fixed position in space, this concept is not strictly accurate. The individual atoms or ions have a certain degree of latitude and have freedom of movement about a so-called equilibrium position. The extent of these vibrations is extremely small but is nevertheless appreciable, considering the minuteness of the atomic scale.

The degree of vibrational movement is markedly affected as the temperature is increased. The amplitude of the oscillation about the equilibrium position increases until at some point an ion or atom will escape from the restoring influence of its surroundings and the crystal lattice will collapse.

There are two opposite forces acting on an atom or ion within a crystal lattice: (a) attraction, towards a centre of opposite charge in the near vicinity; and (b) repulsion or restoration by other groups or charged centres in the same vicinity. The two forces serve to keep each ion in an equilibrium position or at an average separation distance from others which are in close proximity. A simple schematical representation of the action of the interatomic forces is shown in Fig. XII.4. Within a certain separation distance, the repulsion forces predominate, but if the centres are far apart the force of attraction tends to restore them to an equilibrium position indicated by *a*. There is, however, a small distance (*da*) through which ions can vibrate, and so the interatomic distance varies between the extremes *a* — *da* and

$a + da$ and as these represent points of different energy, for a certain vibrational amplitude (da), an energy change dE_1 will be involved.

This energy term is important because it determines the strength of the bond between atoms or ions in the crystal. Where the resultant-force line (see Fig. XII.4) is steeply inclined, the bond strength or lattice energy will be larger than in cases when the line has a smaller slope.

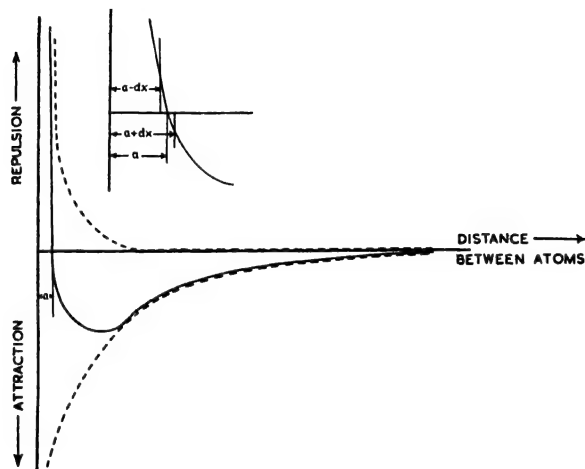


FIG. XII.4. THE FORCES OF ATTRACTION AND REPULSION BETWEEN ADJACENT ATOMS IN A CRYSTAL
The solid line indicates the resultant

In the neighbourhood of the equilibrium position or zero point (a) of the resultant-force line of Fig. XII.4, the curve undergoes a change in character. At shorter interatomic distances, the repulsion forces between ions rise steeply whilst, when the equilibrium position is exceeded, the forces of attraction also increase, but at an ever-decreasing rate. Therefore, as the amplitude of vibration increases, the repulsion and attractive forces around the zero position become unsymmetrical and the restoring force is greater from the $a - da$ extreme than from the $a + da$ point. As a result, the mean centre of vibration tends to be displaced towards a greater interatomic distance and this will become increasingly so as the amplitude extends. The crystal, therefore, expands and the volume increase is thus related to the relative slopes of the resultant-force line on each side of the equilibrium position and to the temperature, which governs the magnitude of the vibrations.

Megaw¹ has investigated the thermal expansion of crystals in relation to their structure and has been able to account for the properties of simple compounds on a quantitative basis. She also explains the anomalous behaviour of more complex types on the basis of different bond characteristics within the same crystal, or the possibility of rotational movement of linkages which supplement or disguise true vibrational effects.

¹ Megaw, H. D., *Z. Krist.*, 100, 58, 1939.

The strength of the bond between adjacent atoms or ions in a lattice is related to the charge or valency of the ion divided by the number of ions of opposite charge which surround it. This concept was first advanced by Pauling and the value (q) is known as the electrostatic share of the ion. (For a more detailed explanation see Chapter II, p. 86.) Megaw has shown that for simple crystals, the coefficient of expansion (α) is inversely proportional to the square of the electrostatic share, i.e.

$$\alpha = \frac{C}{q^2} \quad \text{or} \quad \alpha q^2 = \text{a constant}$$

This relationship holds only for such minerals as the alkali halides, although, if only one type of bond is present in the crystals, the expansion coefficient of more complex substances decreases with increasing bond strength as shown in Table XII.IV and αq^2 is approximately constant.

TABLE XII—IV. RELATIONSHIP BETWEEN
BOND STRENGTH (ELECTROSTATIC SHARE) AND THE
THERMAL EXPANSION COEFFICIENT¹

<i>Mineral</i>	<i>q</i>	$\alpha \times 10^{-6}$	$\alpha q^2 \times 10^{-6}$
NaCl	1/6	40	1.11
CaF ₂	1/4	19	1.19
MgO	1/3	10.5	1.17
ZrO ₂	1/2	4.5	1.12
BeO	1/2	5.1	1.26
Al ₂ O ₃	1/2	5.1	1.26
SiO ₂	1	0.5*	0.50

* Figure for silica glass. The low temperature forms of the silica minerals have a large expansion due to rotational effects and changes in the bond angles.

Hummel¹ has compared the thermal expansion characteristics and the crystal structure of many natural minerals and suggests that those with the same crystallographic symmetry have similar coefficients. Magnesium oxide, for example, has a cubic structure based on rock salt (NaCl) and these two minerals have expansion coefficients of 10.5×10^{-6} and 40.0×10^{-6} respectively. CaO, BaO, FeO and many others have a similar structure and all are characterised by a large thermal expansion.

BeO and Al₂O₃, have an hexagonal structure but are still close-packed, hence the expansion coefficient is relatively high (*circa* 5.1×10^{-6}). Silicate minerals are lower, primarily because the SiO₄-grouping, which usually predominates, has a high bond strength. Framework structures based on three-dimensionally linked SiO₄-tetrahedra should have the lowest expansion coefficients, but such lattices are not close-packed and rotational movements and bond angle changes may occur, which cause large volume changes (see Table XII.XI). At high temperatures, however, when vibrational effects are involved, such minerals have only slight or even negative expansion coefficients. Hummel² concluded that if such high temperature

¹ Hummel, F. A., *J. Amer. Ceram. Soc.*, 33, 102, 1950.

² Ibid. *J. Amer. Ceram. Soc.*, 34, 235, 1951.

structures could be stabilised, a material of low thermal expansion would result, and he synthesised the lithium-alumino-silicates, β -eucryptite and β -spodumene. Both of these have a structure which is based on that of high or β -quartz with aluminium ions replacing silicon, and lithium ions filling holes in the lattice thus preventing inversions. Both minerals have an extremely low expansion; in fact, the former has a negative coefficient in the temperature range 0–1000° C.

Although the simple concept of heat affecting the vibrational movement of bonds within the crystal lattice is far from a complete explanation, many useful conclusions may be derived. As Austin¹ has pointed out, it offers an explanation as to why the expansion coefficients, heats of formation and melting points of simple materials are related. Furthermore, the variation in thermal properties along different crystallographic axes in a substance may be readily explained on this basis.

The thermal properties of a composite material such as are encountered in ceramic studies are influenced not only by the mineral forms which are present, but also by the texture of the body itself. It is understandable, therefore, that the theoretical considerations which have been deduced for simple crystalline substances, must be used with caution in ceramic materials.

The coefficient of expansion of crystals is constant along all crystallographic directions (p. 92) only in those of the cubic variety. Because most ceramic materials are composed of a mass of small crystallites randomly arranged this has little significance, but where large crystals are present or where there is some degree of orientation, the amount of expansion in different directions may vary.

Where more than one type of mineral is present in a material, the coefficient of expansion of the mass is roughly the average of the components, but any porosity in the composite body will have an important effect.

The texture of the body has a pronounced effect on the coefficient of expansion of a material, but only insofar as the porosity reduces the total mass of the material and hence the overall thermal expansion will be lowered. In some cases, a small amount of pore-space in a body will influence the expansion to a very great extent; this is often true in partially-crystallised glasses particularly when cristobalite has formed. On cooling through its inversion point, cristobalite contracts away from the surrounding glass leaving a small amount of void space. When such a specimen is reheated the large volume change associated with the $\alpha \rightleftharpoons \beta$ cristobalite inversion is not apparent because the crystals expand into the void space formed during cooling and do not influence the overall size of the material to any great extent.

The influence of porosity on the thermal expansion of fired clay bodies is illustrated in Table XII.V.

The reversible thermal expansion of materials which react during firing can only be measured at temperatures below that at which reaction occurs, otherwise part of the volume change indicated will be permanent.

Clays. Kaolin and bauxitic fireclays have, after calcination, according to Houldsworth and Cobb, a regular reversible expansion which does not vary much with the temperature of calcination.²

They found that fireclays calcined at Cones 14–20 have a regular reversible

¹ Austin, J. B., *J. Amer. Ceram. Soc.*, 35, 10, 1952.

² Houldsworth, H. S. and Cobb, J. W., *J. Soc. Glass. Tech.*, 5, 36, 1921.

expansion similar to kaolin as most of the quartz is then destroyed by interaction with the fluxes present. The regular expansion is most readily attained with fine-grained and rather fusible materials, whilst it is retarded in the presence of a large amount of quartz.

Fireclays and glass-pot mixtures calcined at Cones 06-9 show a large expansion on heating between 500° and 600° C., according to Houldsworth and Cobb, on account of the quartz present, and on cooling the contraction is larger than the corresponding expansion. The expansion between 100° and 250° C. after calcination at Cone 9 also exceeds the average.

Table XII.V shows the coefficient of expansion of various kinds of clays after calcination at various temperatures.

TABLE XII—V. COEFFICIENT OF EXPANSION OF CLAYS
(Houldsworth and Cobb), coeff. of Exp. $\times 10^{-8}$

Substance	Temperature Range, ° C.	Temperature of Firing prior to Test			
		Cone 06	Cone 9	Cone 14	Cone 20
Kaolin	100-250	—	764	578	—
"	15-1000*	402	531	477	441
Farnley fireclay	100-250	—	1023	875	—
" "	15-500	481	769	676	—
" "	500-600	1331	1275	1075	—
" "	600-1000*	217	183	250	—
" "	15-1000*	491	583	540	305
Ball clay	15-500	542	—	—	—
" "	500-600	980	—	—	—
" "	600-900	431	—	—	—
" "	15-1000*	554	575	436	—
Ayrshire Bauxitic clay	{ 100-250	—	726	652	—
" "	{ 15-1000*	480	605	561	418
Glasgow fireclay	100-250	—	986	801	—
" "	15-500	401	745	542	—
" "	500-600	1276	1220	886	—
" "	600-1000*	279	294	346	—
" "	15-1000*	457	611	554	395

* 600°-900° C. and 15°-900° C. for the Cone 06 specimens.

The effect of porosity on the coefficient of expansion of fireclay is shown in Table XII.VI due to Houldsworth and Cobb.¹

The effect of increasing the porosity of a body is to decrease its coefficient of thermal expansion at all temperatures. Fireclay which has been fired to Cone 9 has a greater expansion at a particular porosity in the range 15°-500° C. than has the same material fired to Cone 06; this trend is reversed in the expansion coefficient over the range 500-600° C. The amount of residual quartz in fireclay fired to 06 is relatively high and, because of the expansion accompanying the $\alpha \rightleftharpoons \beta$ inversion at 573° C., the coefficient of expansion in the range 500°-600° C. is high, but firing to Cone 9 converts some of the quartz to cristobalite or tridymite, thereby reducing the expansion in the range 500°-600° C. but increasing that at low temperatures. The

¹ Houldsworth, H. and Cobb, J. W., *J. Soc. Glass Tech.*, 5, 36, 1921.

higher temperature of firing produces a greater proportion of glass which is highly siliceous and hence confers a lower thermal expansion at high temperatures.

The average expansion of a well-burned firebrick when heated to 1300° C. is about 0.000006 per 1° C.

The coefficient of other non-vitrified claywares is similar to that of firebricks. Mellor¹ found the coefficient of expansion of various kinds of tiles to be 70×10^{-7} per 1° C. on average.

Vitrified Claywares. The coefficient of expansion of vitrified claywares varies considerably according to their nature and the extent of vitrification, but is generally less than that of non-vitrified claywares.

TABLE XII—VI. EFFECT OF POROSITY ON THE COEFFICIENT OF EXPANSION OF FIRECLAY

Temperature of Calcination	Porosity	Coefficient of Expansion $\times 10^{-8}$			
		15°–500° C.	500°–600° C.	600°–1000° C.	15°–1000° C.
Cone 9	28.7	769	1275	183	583
	44.6	602	1053	281	517
	50.2	550	997	295	491
Cone 06	31.7	481	1331	204	455
	47.7	441	1220	211	426
	62.7	406	1203	195	401

Much work has been done on the coefficient of expansion of porcelains and the influence of the various components on this property have been studied. Much of the evidence is apparently highly conflicting but many of the anomalies can be resolved by considering the reactions which take place during the firing.

The major constituents of porcelain are: (a) felspar; (b) flint; and (c) clay; at high temperatures these react to form liquid and other mineral varieties, so that, on cooling, the body is composed of crystals which are mainly mullite and cristobalite with some felspar and glass. The proportion of each component is governed by the proportion of the original constituents and the conditions of firing and cooling in the kiln.

In general, the crystalline components of porcelain will have a higher coefficient of expansion than that of the glass, but the glass itself will have varied expansion characteristics which will depend largely upon its composition; glass rich in silica has a low thermal expansion, but as the proportions of alkali elements and alumina in it are increased, the coefficient increases as also does its tendency to crystallise on cooling.

Porcelains low in felspar have a relatively large proportion of crystals in them because the flux content is insufficient to form an extensive amount of liquid at the temperature of firing. Consequently, the expansion coefficient of such bodies is high, but it may be decreased by adding more felspar to reduce the proportion of

¹ Mellor, J. W., *Trans. Eng. Cer. Soc.*, 5, 153, 1905–6.

crystalline phases. Beyond a certain limit of felspar addition, the coefficient increases again due to the formation of a less siliceous glass and an enhanced tendency for the liquid which forms to crystallise on cooling. This is illustrated in Table XII.VII which shows the change in expansion brought about by increasing the felspar content at the expense of clay, keeping a constant amount of flint.

Additions of clay to a felspar-flint mixture decrease the expansion when small amounts are incorporated, but the alumina in clay increases the tendency to liquid formation and stabilises the glassy phase. Larger amounts of clay increase the coefficient of expansion of porcelain because the total amount of felspar is thereby reduced and more crystals will form. The addition of more clay to a porcelain within the normal composition range tends to increase its coefficient of expansion slightly.

TABLE XII—VII. EXPANSION CHARACTERISTICS
OF PORCELAIN MIXTURES

<i>Composition by weight</i>			<i>Coefficient of Expansion</i>
<i>Flint</i>	<i>Felspar</i>	<i>Clay</i>	
30	7	63	65×10^{-7}
30	31	39	40×10^{-7}
30	49	21	70×10^{-7}

The addition of flint to a porcelain body may either decrease or increase the coefficient of expansion depending on whether the extra flint enters the liquid phase at high temperatures thereby producing more siliceous glass or whether it crystallises to cristobalite.

The hard porcelain with the lowest thermal expansion corresponds to a mixture of 30 per cent flint, 30 per cent felspar and 40 per cent of clay which has a coefficient of 39×10^{-7} (0° – 1000° C. temperature range).

The expansion of porcelain is not regular at all temperatures, which is due in part to the presence of cristobalite with an inversion at about 220° – 280° C. Where quartz is used instead of flint an increased expansion between 550° – 600° C. is often apparent.

Stoneware has a somewhat greater expansion than that of porcelain, but this is due almost entirely to the presence of free unchanged quartz or to a greater proportion of cristobalite.

Glazes must have a coefficient of expansion very similar to that of the body to which they are attached, otherwise serious manufacturing faults will arise. When cooling a glaze from its maturing temperature, there is no sudden arrest or change in characteristics due to crystallisation; the liquid gradually increases in viscosity and only becomes brittle hard in the range 500° – 700° C. Consequently any strain which may be imposed upon it by the differential contraction of the body to which it is attached can be readily accommodated by the glaze at temperatures above a dull red heat. Below this temperature, however, should there be a difference in the coefficients of expansion of the body and glaze, stresses will be set up; if the body contracts more than the glaze (i.e. if its coefficient of expansion is greater), the glaze

will be put into compression and *peeling* may occur. On the other hand, if the glaze has the greater contraction, it will be put into tension and *crazing*, characterised by fine hair cracks will certainly occur. Glazes are weak in tension but strong in compression, hence it is better to use a glaze which has a slightly smaller expansion than that of the body.

The correct adjustment of a glaze so that its expansion will 'fit' that of a clay body is not an easy matter, because the two materials are very different in both chemical composition and physical characteristics. The use of engobes or several vitreous layers of gradually-changing properties is desirable and necessary in many cases, but, even when these are employed, the thermal expansion characteristics of each vitreous coat must be carefully controlled.

The thermal expansion of a glaze (and of a glass) depends largely upon its chemical constituents; each oxide component contributes a share to the total expansion of the glaze and the total coefficient of expansion (α) can be roughly calculated by adding the contribution of each component thus:

$$a_1x_1 + a_2x_2 + \dots a_nx_n = \alpha$$

where $a_1, a_2 \dots a_n$ are the percentage by weight of each oxide component in the glaze and $x_1, x_2 \dots x_n$ are factors for that particular oxide.

TABLE XII—VIII. FACTORS FOR CALCULATING THE THERMAL EXPANSION OF GLAZES

Oxide	Linear Coefficient of Thermal Expansion $\times 10^{-6}$	
	Winkelmann and Schott	English and Turner
SiO ₂	2.67	0.50
Al ₂ O ₃	16.67	16.67
B ₂ O ₃	0.33	-6.53
CaO	16.67	16.3
MgO	0.33	4.5
BaO	10.0	14.0
PbO	10.0	10.6
ZnO	6.0	7.0
Na ₂ O	33.33	41.6
K ₂ O	28.33	39.0
P ₂ O ₅	6.66	—

Winkelmann and Schott¹ in 1894 were the first to propose this method of calculating the thermal expansion and other properties of glazes and they drew up a table of factors for the oxides which are most commonly present in glazes. English and Turner² derived factors which are of more general application. They are shown in Table XII.VIII.

Although it is not possible to calculate the accurate coefficient of thermal expansion of a glaze from such factors, they are useful in indicating the approximate value and also they are a valuable guide towards improving a glaze which 'crazes' or

¹ Winkelmann, A. A. and Schott, F. O., *Ann. Physik. Chem.*, 51, 730, 1894.

² See Turner, W. E. S., *J. Amer. Ceram. Soc.* 12, 760, 1929.

'peels' when applied to a particular body. Additions of alkali reduce the tendency to peel but enhance crazing, whilst more silica or boric acid should be incorporated in a glaze which is liable to craze. Care must be exercised in making such changes because they will, at the same time, alter other important properties of the glaze, such as the maturing temperature and fired appearance.

The stresses which develop between body and glaze during cooling and their effect upon the finished article have been the subject of many investigations. Three idealised cases are shown in Fig. XII.5. Glazes which harden about 700° C. usually

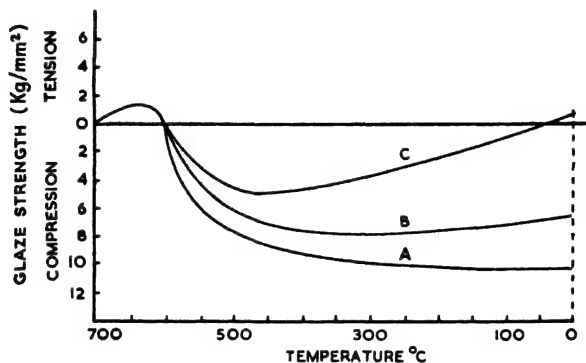


FIG. XII.5.
STRESSES INDUCED IN GLAZES DURING COOLING

- A. Where the body has a much greater coefficient of expansion which may cause peeling;
- B. where the body has a greater thermal expansion than the glaze, but not an excessive one; and
- C. where the body and glaze are of comparable expansion characteristics tending to give crazing

show a small rise into tension on cooling to 600° C., but below this temperature they are put into compression due to the contraction in the body at the quartz inversion. At lower temperatures a high compression may be maintained if the glaze is of low coefficient of expansion (curve A), or if it is of greater expansion, stresses may be reduced, but at room temperature it may still be in slight compression (curve B) or in slight tension (curve C). A body with glaze A would probably 'peel', and glaze C will most certainly 'craze', with glaze B being most suitable. A residual compressive stress of about 5 kg./mm². or slightly above in a glazed body gives the best performance in service.

One of the most serious problems in glazing, especially in ware which is exposed to the atmosphere or to water, is *delayed crazing* which may appear only after many months of use. The cause is considered by Mattyasovsky-Zsolnay¹ to be the expansion of the body due to moisture absorption thereby reducing the compressive stresses in the glaze to a point at which crazing can occur.

The crazing-resistance of a glazed body can be assessed by autoclaving the ware

¹ Mattyasovsky-Zsolnay, L., *J. Amer. Ceram. Soc.*, 29, 200, 1946.

in steam at 50 lb./sq. in., 100 lb./sq. in. or 150 lb./sq. in. Blakely¹ has shown that under such treatments the compressive stresses may be reduced by 5 kg./mm²., and Mattyasovsky-Zsolnay considers that tiles which withstand steam at 100 lb./sq. in. for two hours will not craze in twenty years.

Dunting is another defect in glazed ware which is the result of a differential expansion between body and glaze or between different parts of the body, but unlike crazing it is more localised and appears as a crack or series of cracks in one or more areas of the article. The most frequent cause of dunting is too rapid surface cooling which induces tensional stresses in the glaze or outside layers of the body; for this reason the cooling of glazed ware in the kiln should not be unduly hurried. Dunting may also be associated with hair cracks or laminations in extruded bodies. Bodies containing a high proportion of quartz and those which are soft-fired are more liable to dunting.

TABLE XII—IX. LINEAR COEFFICIENTS OF EXPANSION OF SOME CERAMIC MATERIALS

Coefficient of expansion $\times 10^{-7}$		Coefficient of expansion $\times 10^{-7}$	
Alumina	51	Steatite bodies	70
Beryllia	56	Zircon porcelain	48
Mullite	45	Titanate bodies	80-100
Silicon carbide	47	Magnesite bricks	127
Titanium (rutile)	70	Dolomite bricks	110
Zirconia	45	Chromite bricks	70
Zircon	42	Chrome-magnesite bricks	77
Electrical porcelain	60	Forsterite bricks	90
Cordierite bodies	30		

Shilling is also caused by the incorrect fit of body and glaze. When it occurs the glaze lifts from the surface of the body particularly at sharp edges or corners. Shilling may be caused either by a glaze of too high or too low an expansion relative to that of the body, but more often it is the former and may then be regarded as a type of crazing.

Siliceous materials vary in their reversible expansion according to their origin. Silica has inherently a low coefficient of expansion because of its open structure, but, because of the inversions of various silica minerals, sudden, reversible volume changes may occur at characteristic temperatures in siliceous products (Fig. XII.6).

The coefficient of expansion of natural quartzites, ganisters and silica stones varies between $130-180 \times 10^{-7}$ over the range $0^{\circ}-1000^{\circ}$ C. Above 600° C., however, these materials are virtually volume stable.

Silica bricks expand between 1.0-1.3 per cent linearly between 0° and 1000° C. but 90 per cent of this expansion occurs below 300° C. and is associated with the inversions of cristobalite and tridymite. Bricks rich in tridymite expand less than those with a large proportion of cristobalite.

¹ Blakely, A. M., *J. Amer. Ceram. Soc.*, 21, 243, 1938.

Fused silica has a very low thermal coefficient of expansion; it is only 0.54×10^{-6} or one-twelfth that of ordinary soda glass, so that it is very insensitive to sudden changes in temperature and can be quenched from red heat in cold water without fracture.

Glasses have an expansion which depends on their composition; those rich in alkali elements may have a coefficient of up to 90×10^{-7} . Glasses of low expansion are rich in silica, contain magnesium or calcium oxide as fluxes and amounts of boric oxide or phosphorus pentoxide.

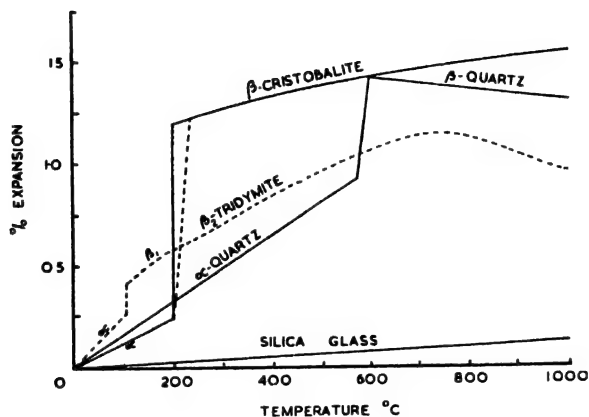


FIG. XII.6. THE EXPANSION CHARACTERISTICS OF THE SILICA MINERALS

Other Ceramic Materials have thermal expansions which depend largely on the minerals which they contain. Table XII.IX shows the linear coefficients of expansion of some minerals and ceramic products.

PERMANENT VOLUME CHANGES ON HEATING

PERMANENT changes in volume differ with the materials in which they occur. The chief change which occurs when ceramic materials are made into various articles and fired is the contraction or shrinkage which occurs when they are heated. Some materials, such as suitable mixtures of clay and silica, are practically constant in volume, whilst others, such as silica, expand when heated and do not regain their original volume on cooling. The extent to which these permanent changes in volume are completed in any given material depends chiefly upon the temperature to which it is heated, so that when firing ceramic materials which are required to have a constant volume when in use, they should be finished at such a temperature as will ensure these permanent changes taking place to the fullest extent.

The principal causes of the permanent changes in volume are:

- (a) The nature and composition of the material.
- (b) Its previous treatment (if any).

- (c) The sizes and grading of the grains.
- (d) The pressure applied in shaping the articles.
- (e) The proportion of water used in mixing the materials.
- (f) The porosity of the material.
- (g) The temperature at which the material has been fired or reheated.

From the above it will be seen that the permanent changes in volume may be divided into two groups:

- (i) Changes which are dependent upon the inherent qualities of the materials.
- (ii) Changes which are dependent on the method of manufacture.

The changes in the first group are chiefly due to: (a) decomposition and the removal of some constituent which causes a reduction in volume, as in the case of clay; (b) the formation of other allotropic forms of the same material which cause a change in the specific gravity and, consequently, either an expansion or contraction; (c) a chemical reaction which produces a new material of greater specific gravity and with consequent volume change; (d) the formation of a liquid phase which flows into and fills some of the original pore space; and, (e) sintering reactions which again result in a decrease in pore space and an overall volume reduction.

The physical causes of change in volume, such as texture, porosity etc., are considered in the respective sections dealing with these subjects.

Whilst it is very desirable it is not always possible to complete the various changes in volume which occur during the firing of ceramic materials, so that a compromise must usually be made, and—where it is important—the maximum permissible permanent expansion or contraction in use should be specified. This is particularly the case with refractory materials, as it is in these that after-contraction or expansion is most harmful.

Clays, when properly burned, shrink permanently to a varying extent, depending on their composition. This contraction or shrinkage takes place in two stages: (a) shrinkage during drying; and (b) shrinkage during burning. The shrinkage in drying is due to the removal of water from the surfaces of the grains and has been described in Chapter IX. The kiln- or fire-shrinkage of clays is due to their decomposition, with the consequent loss of water and the gradual drawing together of the resultant anhydrous grains (and subsequent recombinations and liquid formation). In the case of an earthenware or porcelain, the shrinkage is partly counterbalanced by an expansion due to the transformation of flint and quartz into the low specific gravity forms of silica which have a greater volume than the original materials.

The drying shrinkage of some clay bodies is greatly affected by a small proportion of certain electrolytes and other substances. Thus, the addition of alumina gel, corresponding to adding only 0.2 per cent of alumina, will make it almost impossible to dry some clays, because the expulsion of the water from the gel causes great shrinkage and, therefore, cracking of the ware. Silica gel has a similar, but rather less serious, effect.

The addition of 0.1 per cent of common salt (dissolved in the water used to soften the clay) will halve the drying shrinkage of some clays. Ferric chloride and acids have a corresponding, but stronger effect. With some clays, the addition of

0.15 per cent of liquor ammonia reduces the shrinkage more effectively than any other reagent.

The precise cause of these reductions in shrinkage is not known; it appears to be connected with the colloidal properties of the clay (p. 474).

The shrinkage in clays when fired at high temperatures is mainly the result of the reactions which occur within and between the minerals present. These are of two types as shown in the previous Chapter, namely: (a) crystallisation, in which the amorphous components undergo an internal rearrangement or external combination to form mineral types; or (b) liquid formation, arising from the combination of fluxing elements with the clay body to form low melting-point eutectics. Both reactions reduce the volume of ceramic materials mainly by decreasing the proportion of void space. They will, therefore, be considered in more detail under the heading of porosity changes.

The amount of shrinkage is to some extent dependent on the fineness of particles, finely-grained materials shrinking more than those of coarser grain. This is to be expected, because reactions proceed more rapidly with smaller particles.

This is adequately illustrated, as also is the influence of varying amounts of fluxing minerals by the work of Carr, Hargreaves, Grimshaw and Roberts,¹ who investigated the shrinkage produced in a clay body by differing amounts and various sizes of alkali-bearing hydrous mica. Provided that the grain-size of this liquid-producing mineral was kept constant, the shrinkage produced at 1200° C. was almost directly proportional to the amount present. Finely-divided mica, however, reacted much more readily than coarser material and the resulting volume decrease in the clay was far more pronounced and developed with greater rapidity.

There appears to be little or no fire-shrinkage between 600° C. and 900° C., but above 900° C. the shrinkage increases considerably in amount up to 1100° C. It thus appears that during the burning of the carbonaceous matter scarcely any shrinkage takes place, so that the temperature may safely be raised fairly rapidly between 600° and 900° C. if little carbonaceous matter is present. Shrinkage continues up to the highest temperature at which the clayware is fired and would still continue, if the heating were prolonged, up to the point at which fusion occurs, unless the conditions are such as to cause bloating, when an expansion would result. Consequently, clays will always shrink in use if they are then heated to a temperature higher than that attained in the firing. This is very important in connection with refractory clays, which should be fired at a sufficiently high temperature to prevent an excessive contraction in use.

The presence of non-plastic material, such as grog, quartz or alumina greatly reduces the firing shrinkage of clays, apparently by acting as a non-reactive skeleton during heating. By the addition of such materials an excessive shrinkage in a clay body can be avoided.

Semi-silica bricks containing between 10–15 per cent of alumina and about 80–85 per cent silica are made from inferior ganisters or quartzites to which the requisite amount of a clay is added if necessary. These bricks show little or no volume change during firing or in subsequent service at temperatures up to 1350° C.

¹ Carr, K., Hargreaves, J., Grimshaw, R. W. and Roberts, A. L., *Trans. Brit. Ceram. Soc.*, 51, 345, 1952.

probably because a small proportion of quartz converts to cristobalite and the resulting expansion is sufficient to counterbalance any contraction in the clay.

In Table XII.X is shown the volume changes at various temperatures in clays; the specimens were maintained for two hours at each temperature.

Carr *et al.*, found irregular volume changes in fireclays when heated and were able to associate various effects with the presence of particular minerals. They noted an expansion between 550°–600° C. in clays containing appreciable amounts of free quartz and concluded that where expansion occurred between 600°–800° C., it was due to the exfoliation of hydrous mica.

When an appreciable proportion of fused matter is produced—either as a result of a very high temperature attained or of the presence of fluxes—its effect on the shrinkage is very marked. For this reason, semi-vitrified and vitrified clay wares shrink more than articles made of refractory clays which do not contain much flux and so are only slightly vitrified. As the fusion proceeds, the material, as a whole, shrinks rapidly at first and more slowly later, the amount and rate of shrinkage depending largely on the nature of the flux, soda, potash, and whiting being the most active in this respect.

TABLE XII—X. VOLUME CHANGES OCCURRING ON HEATING CLAYS

	Temperature °C.						
	200	400	600	800	1000	1200	1400
Plastic clay	+0.1	+0.3	+0.3	+0.0	-4.3	-16.2	—
Plastic clay + 30 per cent sand	+0.3	+0.5	+0.7	+0.8	-0.1	-4.3	—
Fireclay (cone 30)	+0.1	+0.2	+0.3	+0.4	0.0	-9.2	-14.0
Fireclay + 20 per cent grog	+0.1	+0.2	+0.4	+0.4	+0.1	-6.3	-9.5
Fireclay + 40 per cent grog	+0.2	+0.2	+0.5	+0.6	+0.4	-3.0	-6.2

As the shrinkage is due to the combination of the flux with the clay, resulting in the production of a molten fluid, any materials which will produce such a fluid will cause the ware to shrink during the firing. Hence, it is scarcely necessary to describe the action of any fluxes in detail, though the following observations may be mentioned:

H. Hope¹ has observed that barium and zinc oxide tend to increase the firing shrinkage of china bodies. Various investigators have noted that mica slightly increases the kiln shrinkage of clay, but if a large proportion of muscovite is present a slight expansion may occur at about Cone 10 (1300° C.). Magnesia and magnesite also increase the shrinkage of clays and also the vitrification range.

Heating at too high a temperature or for a prolonged period may give rise to excessive liquid formation and consequent distortion or squatting in the mass. Bloating and swelling may also occur if gases are liberated in the body when it is maintained at high temperatures. These and other undesirable features of over-burning will be dealt with in more detail later in the chapter.

¹ Hope, H., *Trans. Amer. Ceram. Soc.*, 11, 522, 1909.

Silica bricks expand considerably during the burning, in course of manufacture, on account of the conversion of quartz to tridymite or cristobalite (Table XII.XI), which involves a volume expansion of almost 20 per cent or at least $\frac{7}{8}$ in. per linear foot. The complete conversion is never entirely effected in commercial practice during the firing of the bricks, but a slow and constant expansion continues whilst the bricks are in use at high temperatures, so that if the bricks are to be as constant in volume as possible when in use, they must be heated sufficiently during the first firing to effect as much as possible of the total expansion. Bricks which have not been heated sufficiently during the firing may fail—as the result of continued expansion—when in use.

TABLE XII—XI. SPECIFIC GRAVITY AND
VOLUME CHANGES ACCOMPANYING THE INVERSIONS
AND CONVERSIONS OF SILICA

<i>Temperature °C.</i>	<i>Variety</i>	<i>Specific gravity</i>	<i>Changes into</i>	<i>Specific gravity</i>	<i>Volume increase per cent</i>
Inversions:					
573	α -quartz	2.65	β -quartz	2.60	2
210–280	α -cristobalite	2.32	β -cristobalite	2.21	5
117	α_1 -tridymite	2.28	β_1 -tridymite	2.27	0.5
163	α_2 -tridymite	2.28	β_2 -tridymite	2.27	0.5
Conversions:					
870	β -quartz	2.60	β -tridymite	2.27	13
870	β -quartz	2.60	β -cristobalite	2.21	18
1680	β -quartz	2.60	Fused silica	2.21	18
1470	β -tridymite	2.27	β -cristobalite	2.21	5
1605	β -tridymite	2.27	Fused silica	2.21	5
1719	β -cristobalite	2.21	Fused silica	2.21	0

In the manufacture of high-grade silica refractories for use in steel plant practice, the quartz content after firing must be reduced to a minimum. Burning should continue until the specific gravity does not exceed 2.34.

Bauxitic and aluminous clays shrink greatly when fired during their course of manufacture even though the raw material has been pre-calcined at a very high temperature. It is, therefore, important that bauxite bricks should be properly fired during manufacture, or they may shrink excessively when in use. The chief changes which accompany and probably cause the shrinkage are the decomposition of the bauxite with evolution of combined water, together with a later change due to the recrystallisation of the resulting alumina. The finest grained bauxite bricks usually shrink less in use than those made from coarser materials.

Sintered alumina ware and other oxide compacts may show up to 15 per cent volume reduction during firing due mainly to the decrease in porosity resulting from crystal growth.

Sillimanite bricks usually have a small shrinkage unless the amount of clay added as a binder is excessive. The raw material from which such refractories are made, however, has, in most cases, to be pre-calcined prior to shaping. Three minerals are

in common use for the manufacture of sillimanite ware. These are kyanite, andalusite and sillimanite all of which, on high temperature calcination, change into a mixture of mullite and cristobalite. Sillimanite undergoes little change in density on conversion but andalusite and kyanite show marked increases in volume, the former of 3 per cent and the latter of 20 per cent.

Other refractory wares, such as bricks, crucibles, etc., made of carbon, magnesia, carbides, chromite, zirconia, etc., contract very little during the firing process and have a constant volume when in use. The kiln contraction during manufacture is almost wholly due to the changes in volume of the bond.

The measurement of the permanent volume changes in ceramic materials can be carried out in a similar apparatus to that for the reversible changes (see p. 711). It may also be readily determined from the length or volume changes of a test piece after treatment.

The provisional method for testing the contraction of clay consists in drying the clay at a temperature not exceeding 70° C., crushing it so that it will pass through a 28-mesh sieve, mixing it with water and shaping it into a suitable form, by means of a mould. The test piece is marked with vertical lines 9 cm. apart and allowed to dry, first at the ordinary temperature, then for four to five hours at 70°–80° C., and finally at 110° C. The drying shrinkage is then measured. The test piece is then heated in a furnace at the rate of not more than 100° C. per hour to 900° C., and afterwards at the rate of not more than 4 cones (about 80° C.) per hour to the end of the firing. The test piece is then allowed to cool and is measured. The difference between the vertical lines (*a*) before and after drying gives the drying shrinkage, (*b*) after firing and after drying gives the kiln shrinkage, and (*c*) before drying and after firing gives the total shrinkage. These results are usually expressed as a percentage of the distance between the fiduciary marks before drying the test piece.

Permanent Volume Changes in Fired Bodies may occur if the articles are subjected to heat treatment in service which is sufficient to cause further reactions, e.g. liquid formation. They may occur if the ware is used at a higher temperature than that at which they have been fired in the kiln, or if the soaking period during manufacture has not been sufficiently prolonged.

The *after-contraction* or *-expansion*, as such changes are termed, are important, because unless they are extremely small, excessive length changes may occur on heating in structures made from refractory bricks, thus resulting in cracking or disruption.

Although the importance of volume changes in fired refractory articles on reheating and under service conditions is recognised, there is considerable divergence of opinion as to how the amount of such changes can be predicted prior to the bricks being used. Many firebricks are manufactured to withstand temperatures of 1150°–1250° C. when in use in furnaces, muffles or oven settings; such bricks are normally fired to about 1250°–1280° C. and soaked for 12–24 hours within that temperature range. The user of the refractories must have some means of predicting the amount of volume change which the materials will undergo when maintained perhaps for many months at the operating temperature.

Both the British Standards Committee and the American Society for Testing Materials have specified a Reheat Test for measuring the After-Contraction or

After-Expansion of refractories which involves heating the material to a considerably higher temperature (i.e. 1350°C. or 1410°C.) than would be encountered in practice. It is then assumed that a short period of firing at this elevated temperature would be equivalent to a much longer period of maintained heat at the normal operating temperatures. For some clays, useful conclusions may be derived from such a test, but for a great many others, it is of doubtful value. At 1400°C. , reactions proceed which do not occur at 1300°C. because the equilibrium conditions are quite different. The liquid phase which forms at elevated temperatures is less viscous, so that, especially in porous materials, a shrinkage will occur which would not develop at lower temperatures. Furthermore, at 1400°C. , low-grade fireclays tend to bloat, thereby masking any tendency to contract.

Despite these objections, the Reheat Test is widely used as an indication of the serviceability of a refractory and most users specify a maximum permissible volume or length change.

In British practice the Reheat Test is normally carried out on test pieces $2\frac{1}{2}\text{ in.} \times 2\text{ in.} \times 2\text{ in.}$ cut from a brick or shape. The square ends must be ground as near parallel as possible; a line is drawn down the centre of one long side and the length of the specimen along this line measured with a vernier caliper or some other means which must read to the nearest $1/1000\text{ inch.}$ The test pieces are then placed in a suitable furnace with the long face vertical and fired to 1410°C. and maintained there for two hours. Silica and basic bricks are usually fired to a higher temperature, either 1500°C. or 1650°C. being specified. After cooling, the test pieces are re-measured and the linear change in length calculated.

The A.S.T.M. test (designation C. 113-46) requires that a full brick be used and recommends a five-hour soak at the maximum temperature. Fireclay bricks should be tested at 1200°C. , 1350°C. , 1400°C. or 1600°C. depending upon their proposed application.

When the shrinkage by volume is to be determined accurately, a volumeter such as is used for porosity determinations (p. 408) must be used, the volume of the sample being determined before and after the test and the percentage of volume change calculated from these figures. The expansion of bloating bricks used in steel ladles and as casting-pit refractories can be determined in a similar manner.

Standard Specifications for aluminosilicate refractories as used in the Gas and Coking Industries require that a maximum after-contraction should not be exceeded in the various grades of materials. Details of these specifications are given in Table XII.XII.

Although the Reheat Test affords a rapid and simple method of measuring the probable behaviour of refractories when in use, a more accurate and reliable indication is given by observing the changes in length of a specimen when maintained at a suitable temperature (corresponding to that encountered in practice) for varying periods of time. The rate of the change in length can thus be calculated and extrapolated to infinite time. An apparatus such as that described on p. 711 is most suitable for these tests.

Mellor has shown that if it is assumed that the change of contraction during the firing is proportional to the square of the contraction which has yet to take place, the

effect of repeated heating at 1120°–1160° C. (Cones 2a–4a) approximately follows the law for bimolecular reactions and the contraction may be calculated as follows:

$$x = \frac{a^2kt}{1 + akt}$$

where x is the contraction after any number of firings t , a is the maximum contraction after an indefinite number of firings, and k is a constant depending on the nature of the material. He found that fireclay bricks contracted more in a reducing atmosphere than in an oxidising one. The increased contraction is probably due to the greater fluxing effect of the iron in a reducing atmosphere.

TABLE XII—XII. SPECIFICATIONS OF THE GAS AND COKING INDUSTRIES FOR ALUMINO-SILICATE REFRACTORIES (1955)

	Grade A	Grade D	Grade E	Grade F	Grade G	Grade H
Composition	Silica not less than 94% SiO ₂	Semi-silica 78–85% SiO ₂	Firebrick less than 78% SiO ₂	Firebrick less than 78% SiO ₂	Firebrick more than 37% Al ₂ O ₃	Aluminous firebrick not less than 40% Al ₂ O ₃
Reheat test	1450° C. 2 hr.	1350° C. 2 hr.	1350° C. 2 hr.	1410° C. 2 hr.	1410° C. 2 hr.	1410° C. 2 hr.
Maximum change in size permitted (per cent)	Exp. less than 0.5	–0.50* +1.00	S. 1.20† L. 1.50	S. 1.00 L. 1.25	0.8	0.5
Minimum refractoriness (Cone No.)	31	28	28	30	32	33

* Semi-silica for coke oven usage must not change linearly by more than ± 0.5.

† In Grade E and F material the specifications for large (i.e. where each dimension is at least 6 in.) and small sized blocks are different.

A noteworthy expansion or contraction is very harmful in the case of retorts, and should specially be avoided by using suitable materials and burning them at a sufficiently high temperature. To avoid troubles which would otherwise occur, the Institution of Gas Engineers specifies that a test piece 4½ inches square, cut from a clay retort, when heated at 1350° C. (Cone 12) for two hours should not contract more than 1 per cent in length. It is also important that the reversible expansion or contraction of retorts when in use should also be as low as possible, as it is the changes in volume of the retort whilst it is hot which are one of the chief causes of its disintegration. This is avoided in some bricks, retorts, etc., by using a siliceous clay in such proportions that the expansion of the silica is neutralised by the contraction of the clay, and, consequently, the material is almost constant in volume (see *Semi-silica Bricks*, p. 725).

Silica bricks occasionally show an after-expansion due to the conversion of some quartz which was unchanged during kiln firing, and sometimes to a change from cristobalite to tridymite. The after-expansion measured at 1500° C. may be as high

as 6 per cent in some bricks and it is important that this should be determined so that an expansion allowance can be made when constructing a furnace from them.

Basic bricks, provided that they have been well-fired and that they are made from high-quality materials, rarely show a pronounced volume change when heated to 1500° C. for two hours. A small contraction (*circa*. 0.3 per cent) is not harmful and can be attributed to the sintering of one or more of the crystalline components such as periclase or spinel to form a mass of lower porosity.

CHANGES IN POROSITY ON HEATING

THE porosity of a material has been defined in Chapter VII, as the total proportion of the pores, voids or interstices which occur in a body or agglomerated mass.

In the unfired material, the porosity is related solely to the size and shape of the grains and the manner in which they are blended together, but on heating, the nature of the materials comprising the mass has a very important influence because of the chemical reactions and partial fusing which occurs. The fineness of grain is an added factor in porosity changes at high temperatures but only in so far as it increases the rate at which reactions take place. In this respect, it is interesting to compare the influence of particle-size on the porosity in the raw and fired states. Mixtures of fine materials have a large surface factor and are invariably more porous in the raw state than those containing coarse materials. At high temperatures, however, small-particled material fuses more readily than coarser grained bodies. The liquid formed fills the interstices and voids in the mass thus reducing the porosity.

The porosity of a body may increase or decrease as the temperature is raised, depending largely on the composition and minerals which are present.

Materials Increasing the Porosity. In general, the porosity of a mass will increase if it contains components which volatilise, evaporate or decompose with gas liberation at a particular temperature. Thus, in the drying of moulded ceramic bodies, water is driven off from the pores between the solid particles. Maximum porosity may only be reached in the initial or smoking period of kiln firing, because it is at these elevated temperatures that the last traces of water are removed (see p. 668). Although the removal of water may cause minor rearrangements in the dispositions of individual particles, provided the moisture content is below the critical point (see p. 509), the water lost on drying and firing is entirely replaced by air.

If carbonaceous or other organic constituents are present the porosity will increase when oxidation or burning occurs. Light, porous bodies can be artificially produced by incorporating some combustible, such as sawdust or finely powdered coke or coal, prior to shaping. Naturally-occurring porous materials, such as expanded vermiculite, kieselguhr or diatomaceous earth may also be admixed with clay to produce a similar effect.

Decomposition reactions involving gas liberation can also cause an increase in the porosity of the mass. The destruction of the clay minerals and other hydrous substances, combined with the dissociation of carbonates tends to give a maximum void space in clay bodies at about 800° C.

Materials Reducing the Porosity. The materials which cause a reduction in the porosity of fired articles, partly or wholly composed of clay, are mostly fusible at the

temperature of firing, or they are *fluxes* which combine with some of the other constituents to form a liquid, which fills the pores of the materials. The amount by which the porosity is decreased depends upon the type of fluxing elements, the form in which they are present, the grain-size of the minerals which contain them and the temperature at which the body is fired.

TABLE XII—XIII. EFFECT OF FLUXES ON POROSITY
(after J. Keele)*

Size of Particles of Felspar	Felspar	Porosity in dry State	Temperature of Firing in Seger Cones						
			05	1	3	5	7	9	12
40-mesh	Per cent								
	40	31.00	34.50	30.95	27.55	23.65	19.60	10.95	4.96
	30	33.63	37.30	31.70	28.55	25.40	21.70	14.40	9.33
	20	36.60	40.00	37.15	32.00	30.00	25.40	18.45	14.21
	10	39.50	43.00	40.00	35.70	32.35	30.50	23.00	18.65
100-mesh	40	32.85	36.50	30.80	23.80	17.10	13.20	6.60	1.40
	30	35.20	39.00	38.30	29.40	25.05	18.30	10.80	4.92
	20	37.00	41.00	38.40	30.60	27.50	27.10	14.40	8.87
	10	39.20	42.70	38.15	34.55	32.25	25.30	23.95	16.37
200-mesh	40	35.10	38.60	22.65	18.50	14.80	6.00	—	—
	30	36.45	40.00	28.80	20.50	15.80	13.65	4.40	—
	20	38.05	41.55	33.60	28.45	23.70	21.90	10.50	7.11
	10	41.10	43.80	36.70	33.15	28.25	27.08	17.20	12.75

* *Trans. Amer. Ceram. Soc.*, 13, 731, 1911.

Because alkalis form a liquid with alumina and silica at much lower temperatures than other fluxes, it is to be expected that they would be the most effective in reducing porosity, but because they are usually present in clay bodies as mica or felspar they do not readily react unless the minerals are finely divided. Lime is usually present in clays as calcium carbonate which decomposes at about 800° C. to leave calcium oxide in a readily available and highly reactive form. Hence in many cases lime appears to be a more active flux than the alkalis.

The temperature of firing largely determines the amount of liquid which forms in a clay body containing fluxes, hence the porosity of an article tends to diminish when it is fired to higher temperatures.

Table XII.XIII shows the effect on the porosity of china clay to which are added varying amounts of felspar of three grades and then fired to different temperatures.

The reduction in porosity is greatest with large amounts of felspar of small grain-size and after firing to the highest temperature.

The heat treatment to which materials are subjected also influences their porosity. Burned articles usually have a greater porosity than unfired materials up to the temperatures at which vitrification commences. Articles which have been fired to higher temperatures may be less porous and in some cases are impermeable.

The 'marls' used for blue bricks afford a good illustration of this; in the dry state they are moderately porous, when fired at about 900°C . they have a porosity of about 15 per cent by weight; but after firing and 'blueing' at about 1300°C ., they absorb less than 1.0 per cent of water.

The porosity of articles made of clay increases as they are heated until a temperature of about 750° – 850°C . is reached. During this heating the clay shrinks and reduces the porosity, but the loss of water and carbonaceous matter, which occurs at the same time, is greater than the shrinkage, so that the porosity increases. At the moment when clay is dehydrated (about 450° – 500°C .), the dissociation of the material and the liberation of the combined water increase the porosity by about 10 per cent. At 700° – 800°C ., the porosity depends partly on the initial porosity of the mass and partly on the amount of carbonaceous matter present. In the manufacture of light, porous bricks, in which a large amount of carbonaceous matter has been incorporated, the porosity rapidly increases as this material burns away. When the temperature is increased above 900°C . partial fusion occurs and the molten matter so produced begins to flow into the pores. If the temperature is sufficiently high and the heating is sufficiently prolonged the fused matter will fill all except the closed pores and a non-porous product will be formed. With most clays the article will lose its shape before this stage is reached, but not in the case of vitrified engineering bricks, porcelain, and some stoneware.

Certain types of clays are reduced in porosity after moderate firing temperatures but, as the temperature is raised further, bloating of the mass occurs with an increase in porosity.

Bloating in clays at high temperatures is caused by the evolution of a gas from the body when it contains a large proportion of liquid; a bloated clay has a characteristic honeycomb structure when examined under the microscope. Many gases are liberated at high temperatures and will cause bloating and an increase in porosity provided a sufficient amount of fluxes are also present; sulphur dioxide from sulphates or sulphides, water vapour from micas and other hydrated minerals have both been reported to cause bloating. Nodular ironstone is a serious contaminant of clays because at high temperatures, especially in a reducing atmosphere, it forms localised centres of a highly-bloated, fusible mass, which gives an unpleasing appearance to the brick, in addition to forming areas of high porosity. Although the amount of void space in a bloated brick is large, most of the pores are sealed, so that the amount of water absorption may be very small.

Some types of clay increase in porosity after firing to high temperatures because they *exfoliate*. This behaviour is typical of hard, laminated fireclays, especially those which contain a high proportion of carbonaceous matter. The evolution of gas during burning forces open the bedded layers and produces a mass of high porosity. For this reason, it is very difficult to produce a dense brick from some Scottish fireclays although considerable beneficiation is afforded by fine-grinding such clays prior to shaping into bricks.

The porosity of fired ceramic ware can be reduced by the careful control of *grading* especially when the material does not readily form a liquid phase at high temperatures. The influence of grading on the porosity has been described in Chapter VII.

By *increasing the pressure* used in shaping bricks a considerable reduction in porosity can be secured. Higher forming pressures compress the particles of which the body is composed more tightly and at the same time less water is required during shaping. If the pressure during the shaping of bricks is increased from 1,000 lb. per sq. in. to 8,000 lb. per sq. in. the porosity may be reduced by about 20 per cent of its original figure. The use of still greater pressures would further reduce the porosity but for most claywares the additional expense involved would not be justified. Higher forming pressures are used in the manufacture of high-grade refractory products.

The onset of vitrification or the development of a liquid phase is not the only factor causing a reduction in porosity on firing. Crystal formation may produce a similar effect although higher temperatures are usually required before a sizeable decrease in void space is observed. At elevated temperatures, crystalline minerals begin to form in most ceramic bodies. The first products are often small crystallites hardly visible even under high magnifications; on prolonged heating, however, unless side reactions occur to destroy them, these crystallites start to grow and the mass *sinters* (see p. 635).

As demonstrated in the previous chapter, reactions which occur in clays and other ceramic materials on firing at moderately high temperatures may be (a) destructive or decomposition processes, or (b) constructive or recombination changes, which may be further sub-divided into crystalline development and liquid formation. The relative amounts and importance of the liquid and crystals depend mainly on the composition of the raw material, particularly on the preponderance of fluxing elements. If these are large in quantity, a high proportion of liquid may form, which flows into the pores and, on solidification, gives a mass of low porosity. When crystalline development predominates at normal firing temperatures, the porosity is little changed. There is thus a sharp distinction in property between these two extremes and this fact is well recognised and utilised especially in the manufacture of clay products.

Sintering or crystal growth resulting in large decreases in the porosity of the mass becomes important, however, at elevated temperatures of the order of 1500° C. and above, as in the manufacture of pure oxide refractories for special purposes. Compacts of materials such as finely-divided magnesia, alumina, zirconia, beryllia, etc., may be fired at temperatures well below their melting point and form bodies of low porosity and great strength. The void space within such bodies is reduced by a physical process involving only solid state reactions (see p. 636), which increase in activity as the temperature is further raised or maintained.

Burned clay-wares may be divided into two classes, according to their porosity, as follows:

1. *Porous ware*, including bricks, tiles, terra-cotta, refractory ware, coarse pottery, and earthenware.
2. *Impermeable ware*, including stoneware, china ware, and porcelain.

These divisions are only general, however, as some bricks are quite impermeable to water, and some china ware is appreciably porous.

Building bricks should be moderately porous, as otherwise when moisture

condenses from the air, the resultant water collects in drops on the inside of the walls, producing damp spots. If the pores are sufficiently minute, the bricks may be as highly porous as possible; the more porous they are, the better will the walls 'breathe'. Bricks with large, coarse pores should be avoided, as they admit rain-water too easily, but do not always part with it readily, so that walls in which they are used often remain permanently damp. The porosity of ordinary building bricks should not usually exceed 20 per cent by weight or 50 per cent by volume. Common red bricks and facing bricks usually have a porosity of 5-10 per cent by weight or 12-20 per cent by volume, whilst wire-cut bricks, rubbers, and gault bricks usually have a porosity of 12-20 per cent by weight and 30-55 per cent by volume.

In the south of England, the average amount of water absorbed by bricks during complete immersion is about 12 per cent of the weight of the brick. North of the Trent and in Wales, denser bricks are usual and the average water absorption is seldom above 8 per cent of the weight of the brick. Bricks made by the semi-dry process—that is, by compressing the clay in the form of a damp dust—usually absorb only about 5 per cent of water, though they vary greatly in this respect. For all ordinary purposes, therefore, it is not desirable to designate bricks which absorb less than 15 per cent of their weight of water on immersion as particularly porous. Good bricks should absorb water slowly and should part with it readily when exposed to a dry atmosphere.

Bricks and other articles which are required to resist chemical action at ordinary or moderately low temperatures, or which must possess great strength, must be denser than ordinary architectural materials. Blue bricks of good quality usually have a porosity of only 0.1-2 per cent; it should not generally exceed 3 per cent by weight.

The large hollow blocks used in fireproof floors, etc., are usually made of a highly porous material. This reduces the cost of carriage and the weight of material in the structure, and provides insulation.

Tiles, terra-cotta and other unglazed argillaceous building materials should have a similar porosity to building bricks, but the exposed surface should be non-porous. The best roofing tiles have a porosity between 3 and 18 per cent, light red tiles may have a porosity of 10-18 per cent, and the darkest and densest red tiles a porosity of 3-5 per cent.

With roofing tiles, the porosity is of minor importance compared with the permeability. So long as the tiles will not allow water to pass through them in the heaviest storm, the more porous they are the better, as porous tiles dry more rapidly than dense ones and are more resistant to sudden changes in temperature.

Other *unglazed wares* should have a porosity corresponding to the purpose for which they are to be used. Such articles as flower-pots, filters, etc., must be very porous.

Refractory Articles. The porosity of *fireclay bricks* is often much more important than in bricks which are not heated to a high temperature. It varies very considerably according to the purposes for which the bricks are to be used, but is generally between 8 and 24 per cent by volume or 3-9 per cent by weight. Where there is little corrosion or abrasion, a highly porous brick may be quite satisfactory and, even where these actions do occur, a porous brick may be necessary to give the requisite resistance to sudden changes in temperature.

Porous fireclay bricks containing iron spots, when heated to redness, decompose carbon monoxide liberating free carbon. This is undesirable especially in gas producers, etc., used in the production and utilisation of carbon monoxide gas.

In general, when the articles are to be heated to a high temperature they should be as porous as is consistent with the other properties required.

Saggars should generally have a porosity of 10–40 per cent by volume or even greater, provided that the pores are very small and do not allow the fire-gases to enter into the interior of the saggar and so discolour the goods, and that the saggars possess sufficient strength.

TABLE XII—XIV. PHYSICAL PROPERTIES OF FIRED CERAMIC PRODUCTS

	True S.G.	Bulk Density	Porosity (by volume)
Building bricks	2.4–2.8	1.6–1.95	10–35
Tiles	2.4–2.7	1.4–2.0	3–18
Fireclay bricks	2.5–2.7	1.9–2.1	20–30
Porous fireclay bricks	2.5–2.7	1.0+	up to 60
Semi-porcelain bisque	2.45–2.65	1.9–2.2	13–23
Hard porcelain bisque		2.25–2.45	3–9
China ware bisque		2.25–2.45	2–11
Earthenware bodies		1.8–2.0	20–25
Stoneware	2.3–2.5	2.2–2.4	0.5–2.0
Silica brick (cristobalite)	2.34	1.92	21
Silica brick (tridymite)	2.31	1.85	22
Magnesite brick	3.4–3.6	2.6–2.8	19–21
Chrome magnesite brick	3.85	2.8–3.0	22–26
Chrome brick	3.95	3.15–3.27	14–21
Dolomite brick	3.0	2.52	23
Diatomaceous earth	2.62	0.6	73
Fired kyanite brick	3.2	2.0–2.3	22–30

Muffles should have a reasonably porous structure so that they will permit sudden heating or cooling. Muffles which are too dense are not economical in fuel, as they require a much longer time to heat, as well as to fire the goods.

Glass-house pots and *Tank-blocks* should be close-textured internally, and both the inner and outer surfaces should be very dense so as to resist the corrosive action of the molten glass and the flames.

Retorts should have as high a porosity as is consistent with the other requirements, so that they may be resistant to changes in temperature. Too great a porosity must be avoided, however, where resistance is required to fluxes, ash, etc.

The porosity of *silica bricks* may vary very considerably, though the usual limits are 15–32 per cent by volume.

Basic bricks should have a low porosity and a dense structure; this low porosity is necessary because such bricks are used largely under conditions where there is a considerable risk of corrosion by basic slags. Where they are not subject to corrosion, bricks with a porosity up to 40 per cent by volume may be employed. Ordinary magnesite bricks have a porosity of 22–30 per cent by volume, though many Austrian and German magnesite bricks have a porosity of only 18–21 per cent. After a prolonged use at a high temperature, the porosity may be reduced to as low as 10 per cent.

Asbestos bricks are highly porous and, therefore, withstand sudden changes of temperature, but they are not resistant to the action of fire-gases, slags, and other corrosive agencies.

Stoneware should be devoid of porosity, but this is seldom attained, and the commercial articles absorb 0.5–2 per cent of their weight of water. They should not exceed the latter amount.

Porous bisque or *biscuit ware* is an intermediate product in the manufacture of glazed ware. It is fired prior to glazing to give it greater strength in the dipping and decorating processes and to enable the glaze to adhere well to the surface. A suitable porosity is 10–15 per cent by weight. Excessive porosity is undesirable, as too much of the glaze is then absorbed by the ware; this not only wastes glaze, but tends to cause warping and produces a dull surface.

The porosity of some fired ceramic products along with their specific gravity and bulk density is shown in Table XII.XIV.

CHANGES IN PERMEABILITY ON FIRING

PERMEABILITY is closely associated with porosity but the two properties are quite distinct and should not be confused. A permeable body is one which contains a large number of open pores so that gases and sometimes liquids can pass through it, whilst in a porous body the pores may be sealed or open. A body may be porous which is not necessarily permeable.

A permeable body is usually produced if the amount of liquid formation at the temperature of firing has not been very great, or where the grading of the body is poor and large void spaces are present. Permeability may also be induced by incorporating wood fibres or thin splinters in the body which, on burning, leave open channels in the structure.

If a body is to be impermeable but to have a high porosity, the majority of pores must be sealed; whilst some porous articles are often highly permeable, there is no definite relation between the porosity and permeability of a material and a tile may have a true porosity of 25 per cent and yet be impermeable even to gases.

Ordinary building bricks should be permeable to air, so that they may 'breathe', i.e. allow air to pass through them, but they should not be permeable to water, or rain will enter and make the wall 'damp'. If a house is built with solid walls of impermeable bricks it will appear to be damp, because the impervious walls cannot absorb the moisture condensed on them during cold weather. Other argillaceous building materials, such as terra-cotta, etc., should usually have similar properties. Paving bricks should be quite impermeable.

Roofing tiles should be permeable to air, but not to water, or they will allow rain to pass through them and accumulate on or even drop from the underside of the tiles, thereby causing damage.

Filters should be very permeable so that they allow water or other liquids to pass through them at a suitable rapid rate. The pores must, however, be sufficiently small to prevent any 'dirt' or other undesirable solid matter passing through them. A filter may be tested for permeability by noting the amount of water passing through it in a given time (say twenty-four hours).

Saggars and muffles should be porous but not very permeable, or they will not protect the goods from flame, smoke, etc., produced by the fire-gases. This object is attained by having the pores as small as possible consistent with the articles being resistant to sudden changes of temperature.

Retorts should be porous, but not permeable, or much of the vapour or gas produced in them may be lost. This loss may be reduced by regulating the withdrawal of the vapour or gas, so as to avoid the creation of an appreciable pressure in the interior of the retort. In new gas-retorts, permeability is seldom serious, as the formation of a deposit of carbon on the interior soon prevents any loss of gas by permeation.

Blast furnace linings, ladle bricks and casting pit refractories should have a very low permeability to molten metals and slags. For the most part, they should also be impermeable to gases so as to preserve maximum thermal efficiency; sand moulds, however, should be impermeable to liquid metals, but permeable to vapour, in order that occluded gases and entrapped air may readily escape. The permeability of some refractory materials is shown in Table XII.XV.

TABLE XII.XV. PERMEABILITY OF CERAMIC MATERIALS

<i>Type of Brick</i>	<i>Permeability: ccs. per sec. per sq. cm. through slab 1 cm. thick</i>	<i>Type of Brick</i>	<i>Permeability: ccs. per sec. per sq. cm. through slab 1 cm. thick</i>
Fireclay	0.025—0.063	Magnesite	0.065—0.092
Silica	0.040—0.120	Chrome-magnesite	0.030—0.064
Sillimanite	0.010—0.030	Diatomite	0.008—0.080
Alumina	0.028—0.042	Porous insulating fireclay:	0.10 —1.2
Ladle Bricks	0.003—0.062	Glasstank blocks	0.002—0.013

The permeability may vary considerably in different directions in a pressed brick; it is usually greatest in the direction at right angles to the applied pressure.

CHANGES IN THE SPECIFIC GRAVITY

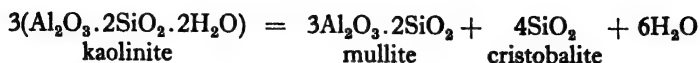
WHEN a material is heated changes also occur in the specific gravity or the density of the body. The true specific gravity of the material of which the body is composed may alter and in addition there may be variations in the apparent specific gravity or bulk density of the shape itself (see p. 408). These latter are the result of changes in the exterior volume and mass of the body.

TRUE SPECIFIC GRAVITY

THE true specific gravity of a material is the average value of the true density of the minerals present. If the proportion of each mineral type can be deduced, the average specific gravity may be calculated by taking the arithmetical mean of the value of the components so that changes which occur on firing are related to those changes in the actual mineral components themselves. Thus a particular mineral

may decompose and then recrystallise or recombine with other components to form entirely different minerals; or liquid may form at high temperatures which solidifies to a glass of a different specific gravity from that of the initial components.

Kaolinite, for example, has a specific gravity of 2.615. On heating it dissociates and finally forms mullite (s.g. 3.03) and cristobalite (s.g. 2.32) in accordance with the following equation:



The weights of mullite and cristobalite in the fired product are in the ratio of 426 to 240. Therefore the final specific gravity is

$$\frac{426 \times 3.03 + 240 \times 2.32}{666} = 2.77$$

Silica is one of the few materials which decreases in density on heating. This is the result of the allotropic changes and the production of low density forms. The recrystallisation of other oxides also results in a change in specific gravity as shown in Table XII.XVI.

TABLE XII—XVI. CHANGES IN SPECIFIC GRAVITY
ON HEATING

	450° C.	1000° C.
Ferric oxide	5.102	5.195
Alumina	3.401	3.729
Chromic oxide	4.933	5.050
Magnesia	2.950	3.674

The true specific gravity of minerals, especially those rich in silica is altered when they are melted and then cooled to a glassy form. Even when only partial fusion occurs the changes in the specific gravity are often much more rapid than at a slightly lower temperature, and the product may be quite different in character, even though its composition (as shown by analysis) is unchanged. Thus, if crystalline quartz is heated to any temperature below its fusing-point its specific gravity cannot be reduced below about 2.3, and that of other siliceous materials of a crystalline nature cannot be reduced below 2.32 or 2.33 even by prolonged heating, provided partial fusion does not occur, yet as soon as sufficient fused material is formed the specific gravity drops rapidly to 2.2. This change in behaviour is due to the transformation, during fusion, from crystalline to the amorphous state; the explanation is confirmed by the fact that flint and other amorphous forms of silica may have a specific gravity as low as 2.2 before fusing, and no sudden change occurs in their specific gravity when the mass melts. The change in specific gravity which occurs on melting various siliceous materials is shown in Table XII.XVII, due to Purdy and Moore.¹

¹ Purdy, R. C. and Moore, A. H., *Trans. Amer. Ceram. Soc.*, 9, 226, 1907.

The rate of cooling often has an important effect on the specific gravity of a material; slow cooling increases the amount of crystallisation from a liquid and thus usually results in an increase in the true specific gravity of the material.

Because the reactions which occur in ceramic materials are slow, even at high temperatures, the maximum temperature attained and the duration of heating also affects the specific gravity.

TABLE XII—XVII. EFFECT OF MELTING ON SPECIFIC GRAVITY

<i>Material</i>	<i>Specific Gravity in Crystalline Form</i>	<i>Specific Gravity in Glassy Form</i>	<i>Reduction in Specific Gravity, per cent</i>
Quartz	2.6630	2.2800	16.3
"	2.6500	2.1900	17.3
Mica	3.0719	2.2405	27.0
Orthoclase	2.5740	2.3280	9.6
"	2.5883	2.3073	10.9
Microcline	2.5393	2.3069	9.1
Albite	2.6040	2.0410	21.6
Oligoclase	2.6600	2.2580	15.1
"	2.6061	2.3621	9.1
"	2.6141	2.1765	16.7
Labradorite	2.7333	2.5673	6.1

When a complex or impure ceramic material is heated, the impurities present may play an important part in changing its true specific gravity by combining with a portion of it to form a fusible material of a different nature and specific gravity from that of the original substance. For example, clays from various sources differ in specific gravity on account of variations in their composition and structure. On heating, these variations cause the clays to act in different ways. Table XII.XVIII shows that whilst ordinary fireclays and most red-burning clays decrease in true specific gravity on firing, some highly-aluminous clays increase in specific gravity.

It will be seen that in the last four clays in the Table, the specific gravity decreases most in the ones containing the largest proportion of flux. In the first seven clays, however, the presence of a large amount of alumina causes variations and in all cases but one, an increase in the specific gravity. The continued decrease in the specific gravity of overburned clays shows that molecular changes are still going on and that equilibrium is not reached at any convenient stage of vitrification.

The true specific gravity of *porcelain* varies from 2.24 to 2.35; the more complete the vitrification the lower will be the specific gravity. The specific gravity of porcelain is also markedly influenced by its composition.

The specific gravity of *earthenware* and *stoneware* bodies also depends on their composition and duration of heating. Earthenware bodies vary between 2.4 and 2.6 whilst stonewares, because they are more vitrified, have a lower value (see Table XII.XIV).

Siliceous Materials. It has previously been shown that the temperature attained, and more especially the duration of heating, is of great importance in the conversion

TABLE XII—XVIII. SPECIFIC GRAVITY OF BURNED CLAYS

	<i>Flux per cent</i>	600° C.	750° C.	900° C.	1000° C.	1100° C.	1200° C.	1300° C.	1400° C.	<i>Change</i>
Ruabon aluminous fireclay	4.24	2.55	2.57	2.56	2.59	2.58	2.52	2.49	2.37	-0.18
Kilwinning	3.05	2.46	2.52	2.55	2.66	2.55	2.56	2.55	2.50	+0.04
Mansfield	2.58	2.45	2.53	2.61	2.65	2.65	2.63	2.53	2.50	+0.05
Stourbridge	2.02	2.50	2.53	2.60	2.64	2.57	2.57	2.63	2.62	+0.12
Kilwinning aluminous shale	1.57	2.53	2.63	2.74	2.72	2.70	2.71	2.72	2.72	+0.19
Halifax	1.14	2.50	2.54	2.50	2.53	2.54	2.57	2.61	2.54	+0.04
Ayrshire bauxitic shale	0.69	2.57	2.64	2.67	2.82	2.75	2.79	2.88	2.88	+0.31
Stourbridge	2.62	2.48	2.51	2.60	2.62	2.52	2.50	2.46	2.33	-0.15
"	1.80	2.50	2.52	2.55	2.60	2.56	2.51	2.49	2.38	-0.12
Halifax	2.42	2.47	2.48	2.37	2.41	2.43	2.48	2.45	2.34	-0.13
Grossalmerode	1.74	2.51	2.64	2.63	2.61	2.60	2.56	2.53	2.41	-0.10

TABLE XII—XIX. EFFECT OF REPEATED HEATING ON SPECIFIC GRAVITY OF SILICEOUS MATERIALS

Material	Specific Gravity											
	Number of Times Heated in Oven											
	Raw	1	2	3	4	5	6	7	8	9	10	11
Quartz from Norwegian pegmatite (in pieces)	2·65	2·38	2·33	2·325	2·33	2·32	2·31	2·32	2·33	—	—	—
Quartz from Norwegian pegmatite (in powder)	2·65	2·37	2·34	2·34	2·335	2·33	—	—	—	—	—	—
Quartz sand from Hohenbocka	2·651	2·591	2·502	2·456	2·450	2·442	2·428	2·386	2·369	2·343	2·338	2·328
Pure geyserite from Taurus	2·651	2·555	2·492	2·478	2·391	2·394	2·366	2·344	2·321	2·316	2·313	—
Average geyserite (ground)	2·651	2·456	2·361	2·349	2·333	2·317	2·306	2·307	—	—	—	—
Quartz crystal (St. Gothard) (in pieces)	2·65	—	—	—	—	2·64	—	—	—	—	2·63	—
Quartz crystal (St. Gothard) (in powder)	2·65	2·568	2·553	2·547	2·519	2·475	—	—	—	—	—	—
Flint (in pieces)	2·632	2·231	2·241	2·248	2·239	2·233	2·255	2·251	2·231	2·230	—	—
Chalcedony (in pieces)	2·607	2·16	2·17	2·17	2·19	—	—	—	—	—	—	—
Hydrated silica (Kahlbaum)	—	2·322	2·319	2·312	2·316	2·317	—	—	—	—	—	—
Quartz glass (Heraeus)	2·21	2·327	2·328	2·33	—	—	—	—	—	—	—	—

of quartz to the low specific gravity forms of silica. Table XII.XIX shows the effect of heating various siliceous materials to a temperature of about 1430° C.

Hugill and Rees¹ have found that the powder density of lime-bonded silica bricks is reduced from 2.65 to 2.40 in the first burning and to 2.35 in four burnings. Even in eleven burnings it is not reduced to 2.30. The porosity falls steadily after the first burning and is constant after seven burnings. The mechanical strength increases about 30 per cent in five subsequent burnings. Crystals of tridymite appear after the second burning, and after eleven burnings most of the silica is in the form of tridymite.

Table XII.XIX, due to Rieke and Endell,² shows the changes in specific gravity occurring when various kinds of silica are repeatedly heated to a high temperature in a hard porcelain oven.

The rate of reduction in the specific gravity of pure siliceous materials on firing depends on the size of the quartz grains, and the relative amount of crypto-crystalline or amorphous silica. Pure quartz converts very slowly, whilst amorphous silica is rapidly changed to cristobalite at 1250° C. The addition of small amounts of impurities, e.g. lime, increases the rate of conversion of quartz (p. 685).

Sillimanite refractories may change appreciably in specific gravity on firing depending on whether kyanite, andalusite or sillimanite is the principal mineral variety in the unfired body. At high temperatures, all these minerals form mullite and cristobalite and the fired material has a true specific gravity of 2.99, so the greatest change will be in kyanite (sp. gr. = 3.59) and less in andalusite (sp. gr. = 3.18) and sillimanite (sp. gr. = 3.08).

Although kyanite has to be pre-calcined before bricks can be made from it, the raw material is a valuable ingredient in some high temperature cements, mortars and linings where the increase in volume caused by its change in specific gravity is of value.

Basic materials such as magnesite and dolomite undergo considerable change in true specific gravity on firing. The amorphous oxides of magnesium and calcium which usually form after low temperature calcination, change to crystalline varieties at high temperatures. Magnesite (magnesium carbonate) in the unfired state has a specific gravity of 2.9–3.1; at about 700° C. it loses carbon dioxide to form amorphous magnesia (sp. gr. 3.23); intense burning in a rotary kiln produces periclase with a true specific gravity of 3.57–3.62 depending on the presence or otherwise of impurities. The change in raw dolomite is less pronounced from 2.85 to about 3.2.

Chrome ores do not change appreciably in specific gravity on firing unless the type of spinel (p. 194) alters due to oxidation or solid solution.

The true specific gravities of some ceramic products are shown in Table XII.XIV.

THE APPARENT OR BULK DENSITY

CHANGES in the bulk density of ceramic materials on heating are dependent on changes in the true specific gravity and the porosity of the mass as a whole; changes in either of these factors will change the bulk density.

The bulk densities of some fired ceramic products are shown in Table XII.XIV.

¹ *Trans. Ceram. Soc.*, 25, 81–90, 1925–26.

² *Silikat Zeitschrift*, 1913, No. 2.

CHANGES IN WEIGHT

MOST ceramic materials change in weight during heating. This is the direct result of reactions which take place with the liberation or absorption of gases.

Weight is lost from ceramic materials in the following ways:

- (a) During drying when adsorbed water is removed.
- (b) In the early stages of kiln firing, when water which is more strongly retained is evaporated.
- (c) By the oxidation or burning of carbonaceous material.
- (d) Through the decomposition of clay and other hydrous minerals. The temperature range over which such reactions occur depends on the mineral type, but is usually between 400–700° C.
- (e) On the decomposition of other minerals, such as carbonates or sulphates.

The amount of weight loss in clays is variable and depends on the relative concentrations of decomposable minerals. Purified china clay loses about 14 per cent by weight at the temperature of reaction of kaolinite. Fireclays and ball clays being less rich in hydrous minerals lose less, in general, although if the concentration of carbonaceous material is high or should hydrates of alumina be present, the average figure of 6–8 per cent may be considerably exceeded. Brick clays, in which the proportion of quartz is usually high, average about a 5 per cent loss, although this may be greater if carbonaceous matter or calcium carbonate is present.

Siliceous materials, once thoroughly dried, undergo little change in weight on heating. The common starting materials for basic refractories are either the carbonate or hydroxide of magnesium or calcium where weight losses of up to 50 per cent occur, hence pre-calcination is necessary before they can be used.

A gain in weight infrequently occurs during the calcination of ceramic materials. This is the result of oxidation of a particular component as, for example, ferrous iron minerals to the ferric form. Sulphides under favourable conditions may be oxidised to sulphates which also leads to an overall increase in weight.

CHANGES IN THE TEXTURE

CHANGES in texture frequently occur on heating ceramic mixtures; in fact, conditions are often designed to effect certain desirable alterations. Texture as defined in Chapter VII is related to the size, shape and grading of the particles which compose the mass. Therefore any changes in these three conditions is tantamount to a change in texture.

A coarsely-grained, open-textured material can be changed through the agency of heat to a homogeneous non-porous structure, e.g. glasses, glazes and porcelain bodies. On the other hand, crystallinity may be enhanced after high temperature heat treatment as in sintered bodies.

Changes in texture are thus related to the chemical and physical processes which occur at high temperatures, i.e. to crystal development and liquid formation.

CHANGES IN OTHER PHYSICAL PROPERTIES

MANY other properties of ceramic and other materials are liable to change as the result of the application of heat. These include simple alteration in the character of the body, such as the feel and hardness (see Chapter XIV) and strength (see Chapter XIII) or they may involve more fundamental features, as for example, thermal, optical and electrical properties (see Chapter XIV).

The changes which occur in the physical properties of a ceramic material are, like the chemical changes which bring them about, slow in reaching completion. This is desirable when, for example, pronounced volume alterations occur, otherwise serious faults might develop in the fired ware. For this reason the rate of heating and cooling must be rigidly controlled, as also must be the maximum temperature of firing and the period of time that the ware is soaked. Failure to observe the conditions will lead to faults in the ware.

EFFECTS OF EXCESSIVE HEATING

WHEN any ceramic material or article is heated under such conditions that it loses its shape, swells undesirably, or undergoes any other changes which reduce its usefulness for the purposes for which it is intended, it is said to be *over-burned*. Over-burning is also said to occur when a material which should be highly porous becomes less so, even though it does not lose its shape. If an undesirable colour is produced as a result of excessive heating, the article or material is also said to be over-burned.

Over-heating may, therefore, be described as any result of heating which enables the reactions which lead to fusion to progress further than is desired in the particular case under consideration. Hence, what may be a sign of over-burning when a material is required for some purposes may indicate the opposite (under-burning) of the material for other purposes.

Over-heating may be due either to the material or article being raised to too high a temperature, to the heating being unduly prolonged or to the heating being repeated too frequently.

Distortion or squatting occurs when the amount of fused material present in a mass is sufficient to cause the latter to change its shape. The cause of this distortion is the mobility acquired by the solid particles in the presence of the molten material, whereby the mass as a whole cannot resist the pressure due to its own weight and, therefore, becomes reduced in height and increased in width until a shape is reached at which the whole mass remains in a state of equilibrium. If the temperature rises still further, or if the heating is prolonged at the critical temperature, more molten material will be formed and still further changes of shape will occur, until eventually the whole mass becomes fluid. The increase in mobility may be due either to the material being heated to too high a temperature, to the heating being too prolonged or the pressure too great. The difference between the temperature at which squatting begins and that at which the whole mass is fused and becomes fluid is termed the *fusion range*, whilst the refractoriness (defined on p. 702) is intermediate between the two extremes of this range.

As particles immersed in or floating on a fluid move more readily when pressure is applied to them, the amount of squatting is greater when a ceramic material is heated under pressure, or, alternatively, the change in shape occurs at a lower temperature because of the increased mobility of the solid particles when under pressure. Hence, the resistance to heat or refractoriness of a material is lower when it is under pressure or supports a load (p. 778) than when it is quite free.

The shape of a mass also affects the temperature at which squatting first appears, a tall mass changing its shape at a lower temperature than a short one, as the pressure on a unit area in the lower part of the latter is much less. The shape of the mass before heating also determines its behaviour after squatting has commenced; thus, Seger cones bend over before becoming wholly liquid.

Boiling, or the conversion of a liquid into vapour or gas, will occur if the liquid is raised to a sufficiently high temperature without it undergoing decomposition. This change seldom occurs in ceramic materials as their boiling points are usually unattainable in commercial furnaces. Glazes sometimes present the appearance of having been suddenly solidified whilst in a state of ebullition, but this is due to a wholly different cause and is quite distinct from true boiling, being caused by the partial escape of moisture or other gases from the ware after the glaze has been fused. A spurious boiling also occurs when clays rich in carbonaceous matter are heated too rapidly, the surface of the clay being sealed with fused material before the gases formed by the burning carbonaceous matter have escaped from the mass.

The **volatilisation** of some of the constituents of ceramic materials may occur at very high temperatures. Thus, the alkalies and some of the silica in clay may be partially volatilised so that when clays are heated repeatedly at high temperatures they become slightly more refractory (see also p. 672).

Mellor¹ found that nearly 20 per cent of the alkalies in an earthenware body were volatilised by overfiring it at 1400° C. Under reducing conditions and in the presence of water vapour, the loss is still greater. Mellor¹ also found that a saggar lost 22 per cent of its alkalies after firing it seven times at 1200° C.

The volatilisation of alkali from some glazes and the resultant dulling of the glaze is mentioned on p. 747.

Silica appears to be appreciably volatile at high temperatures, especially in the presence of carbon, as the latter reduces it to silicon monoxide which volatilises and is again oxidised and re-forms silica. This change of composition does not occur to any very great extent below 1650° C., but at higher temperatures quartz crystals, large enough to be readily seen with the naked eye may be completely volatilised in a reducing atmosphere. In the absence of carbon, silica does not appear to be volatile at any attainable temperature.

EFFECT OF PROLONGED HEATING

VERY little is known scientifically as to the *duration* of heating necessary to produce ceramic articles with certain properties. It should be possible, by correlating time, temperature, and specific gravity, to provide information which will avoid waste of fuel. The amount of non-reversible expansion or shrinkage on reheating should

¹ Mellor, J. W., *Trans. Eng. Ceram. Soc.*, 5, 75, 1906.

provide similar information. Unfortunately, so many other factors are involved that it is difficult to draw sound conclusions.

The effect of a prolonged 'soaking' during the firing of ceramic materials has been described on p. 670. A moderately long 'soaking' is often beneficial, but if it is unduly prolonged, the effect may be deleterious instead of useful, as the production of an excessive amount of fused matter may endanger the stability of the mass or crystallisation may cause a decrease in strength and may render the material brittle or, as in the case of devitrification of silica glass, it may spoil the material for the purpose for which it is intended.

Prolonged heating may also cause excessive shrinkage in clay wares or excessive expansion in siliceous materials, if the finishing temperature during the burning of the ware was not sufficiently high, and these changes in volume may endanger the stability of the mass.

Swelling, bloating, and similar defects may occur as a result of prolonged heating at high temperatures, and if any fluxes are present which can combine with silica or bases, an increased amount of fused material may be produced, so that the effect of excessively prolonged heating may be similar to that of heating the material to too high a temperature and so over-burning it.

As volatilisation of part of the soda and potash may occur if the heating of a glaze is prolonged, this may lead to the glaze becoming dull instead of glossy; undue prolonging of the heating at the finishing temperature of glazes should be avoided.

Excessive heating of a molten glaze in contact with clay will usually enable reactions to occur between them with the result that an unfused product is formed. This destroys the glossy appearance of the glaze and so makes the ware defective. Such reactions are precisely the same as those which occur when a crude clay or pottery body is heated excessively, but the effect being confined more closely to the surface of the ware is more easily observed.

Prolonged heating at a sufficiently high temperature enables the reactions which lead to complete fusion to progress further than if the period of heating were shorter so that its general effect (that of over-burning) is similar to that when these reactions are not arrested at the proper time.

Hence, prolonged heating, whether during the firing in the course of manufacture of the articles or whilst the articles are in use, may be either useful or harmful. If it forms part of the firing process it is generally useful as it increases the strength and resistance to acids and abrasion and reduces the porosity, but if the prolonged heating occurs when the articles are in use, its general effect is harmful, as it tends to increase the amount of fused matter present. For this reason, ceramic materials which require to be heated to high temperatures during long periods should be of a highly refractory nature, or they will eventually collapse through squatting or distortion.

EFFECT OF REPEATED HEATING

WHEN ceramic materials are repeatedly heated and cooled the effect is similar in many respects to that of prolonged heating (p. 746), the same kind of changes taking

place in both cases, but a much higher temperature or a much longer time is required compared with that needed if there has been no cooling.

The effects of repeated heating and cooling also differ according as the treatment is (a) at a rapid rate; and (b) at a slow rate.

The effect of rapid heating and cooling when repeated several times is one cause of the defects known as spalling and shattering (p. 865).

The chief materials which are subjected to repeated heating and cooling are the walls of some kilns and furnaces, saggars, glass-melting pots, retorts, crucibles, etc.

The effect of repeatedly heating *saggars* to temperatures between Cones 8 and 16 (1250° – 1460° C.) is to reduce the strength on account of the strains set up in the material and also to increase the tendency to crystallisation.

A considerable improvement in the life of saggars in recent years has been effected by introducing amounts of talc or steatite in the clay body used in their preparation. Such additions lower the thermal expansion of the fired body and so reduce the tendency to thermal failure, but other factors are also probably involved.

Crucibles, when repeatedly heated, become hard and vitreous as a result of the action of the contents upon the crucible. The resistance of the crucibles to sudden changes of temperature is correspondingly decreased so that after a time crucibles 'perish' and can no longer be used.

When *fused silica* is repeatedly heated at about 1200° C. it shrinks and devitrifies forming tridymite or cristobalite, especially in the presence of basic or alkaline dust or ash.

In all these instances, the effect of repeated heating is to permit the various reactions which lead to ultimate fusion to make further progress to completion and to overcome the arrest of these reactions which occurs when the article or material is allowed to cool for the first time. Repeated heating at a moderately high temperature also facilitates the production of a state of equilibrium by the formation of crystals from a molten or vitreous mass, and, consequently, effects partial devitrification and increases crystal growth.

CHAPTER XIII

STRENGTH AND ALLIED PROPERTIES

THE term *strength* is a very vague one and is used in several ways. The most frequent use of the term 'strength' in connection with ceramic materials is to indicate the ability of an object or mass to retain its shape when various mechanical forces are applied to it under different conditions. In this sense, the strength of a material is due to the cohesion of the particles of which it is composed and the resistance to pressure of the individual grains, especially those forming the coarser aggregate.

If a material fails suddenly when subjected to a sharp blow or other sudden shock, it is said to be *brittle*; if it is easily and gradually crushed it is *friable*, but if it gradually yields under a succession of blows and forms a coherent mass of different shape, it is termed *malleable*. If its shape can be altered by pulling one portion of it or by passing it through a small aperture it is said to be *ductile*, and if it shows great resistance to such treatment or to bending it is regarded as *tough*.

A material which regains its original shape as soon as the applied force is removed is termed *elastic*, and if a hard object after falling on it is caused to rebound to a considerable height the material is said to be *resilient*.

When the shape of a mass can be altered by bending it is said to be *flexible*. Whenever a force applied to a material causes alteration in its shape the material is said to be *deformable*, and the relation of the change in shape to the force applied is known as the deformability of the material.

The term *durability* introduces a time element, and it is measured by the length of time the required property, such as strength or toughness, is maintained. Thus, a material may have a high resistance to crushing when new, but the conditions under which it is used may be such as to reduce its strength in this respect within a short period. Such a material or article could not be regarded as 'durable' under the prevalent conditions.

All these properties are closely related in various ways to the 'strength' of ceramic and other materials. As the strength of any material is due to a complicated series of qualities, different means are employed to express different kinds of strength, and no single figure can possibly represent the strength of an article in every respect. Thus, two materials may simultaneously have a high crushing strength and a great resistance to a tensile or 'pulling' force, yet they may behave quite differently with respect to their malleability or ductility, etc. Consequently, each aspect of the strength of a material must be considered separately, after which the combination of several of these properties may be considered.

Cohesion is the force which holds the particles of a mass together; it may be regarded as the force of attraction between the atoms or molecules of a material, and, according to its intensity, a mass may be rigid like a brick, fluid like water, or it may possess various intermediate characteristics such as malleability, plasticity, etc.

It is closely related to binding power (p. 782). It may range from the slight cohesion of moist sand or soil, produced by a film of water over the particles, to the large cohesion of blocks of carefully dried and burned plastic clay. The cohesion in raw clays and pastes varies with the proportion of water or 'binding power' present, as well as with the packing of the particles and the mineralogical composition of the mass. When a clay or clay-mixture is completely saturated with water the cohesion is zero, but with some very homogeneous clays it is at a maximum when the water present is just short of saturation.

The cohesion of raw clays also increases with a decrease in particle-size and with the presence of organic or colloidal binding agents. Some extremely fine clays, when dry, have a tensile strength greater than that of Portland cement, and a much greater strength after being heated to 1000° C. or above.

The cohesive properties of clays are most highly developed when there is a well-graded mixture of particles of all sizes.

Cohesion is measured by the force required to separate the particles from each other, and, according to the purpose for which the material or article is to be used, its cohesion is judged from its tensile strength, crushing strength, ductility, etc. As the simplest conception of cohesion is the force holding the particles together, it is measured most conveniently as the converse of the force needed to tear them apart, i.e. the *tensile strength*. This is difficult to determine accurately in the case of a soft, plastic paste, but is quite easy with a stiffer paste or a fairly rigid solid, such as a piece of dried or burned clay, and a knowledge of it is often of great value in investigating the properties of ceramic materials at different stages of manufacture or when they are in use. A high tensile strength in a plastic material is very desirable as it facilitates the manufacture. In dried materials, a high tensile strength lessens the risk of damage in handling and in such irregularities of treatment as heating the material too rapidly during the drying or burning. In the production of vitreous ware, such as porcelain, where there is a considerable proportion of fluid present towards the end of the burning process, a high tensile strength at a high temperature is essential, as, otherwise, the distortion of the mass would be so great that many desirable shapes could not be produced.

A high tensile strength is also important in the case of some finished articles, such as the large crucibles used for melting metals; these are lifted out of the furnace with their contents, a pair of tongs being used, and are carried several yards before being emptied. The weight of their contents exerts a great tensile stress, especially as the material of which the crucibles are made is somewhat soft at the temperature of some molten metals. The walls of the 'pots' used for melting glass must also have a high tensile strength in order to withstand the conditions under which they are used. Equally important is the tensile strength of the glazes applied to ceramic materials. The thin film of glaze is subject to complex forces connected with its surface tension and allied phenomena, and unless the glaze is able to accommodate itself to these various stresses it will eventually craze or 'peel'. Glaze with a high tensile strength will stretch considerably before it will crack, and so will provide a permanent protection under conditions where it would be unattainable with a weaker glaze. This characteristic was formerly thought to be best obtained by using glazes with a high degree of elasticity—an idea which seems to be incompatible with such

materials, but R. Rieke has shown that in this connection a high tensile strength is of greater importance than elasticity.

The cohesion of a raw clay is sometimes measured by the force required to drive a blunt steel wedge through a block of clay (as suggested by Atterberg¹). Such force is roughly in inverse proportion to the moisture content of the mass, but there is not a regular progression. In the wet paste the wedge merely cuts, but the drier blocks split suddenly with an irregular fracture. As would be expected the cohesion is dependent on the physical character of the clay-water system at any particular instance and therefore an irregular variation occurs (Fig. XIII.1).

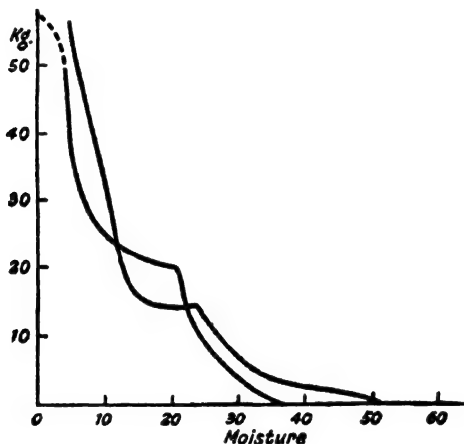


FIG. XIII.1. TYPICAL COHESION-MOISTURE CURVES

Binding power is closely related to cohesion and to tensile strength, but differs from them in at least one important respect. The 'binding power' is that which enables a material to act as a cement or binding agent in uniting particles of other materials to which it is applied or with which it is mixed. The term is used in a special sense in connection with certain ceramic materials, as being that power which enables a plastic clay to be mixed with a considerable quantity of non-plastic material, and to produce a mixture which possesses plastic properties and ample tensile strength for the purposes for which it is required. The binding power of clay is usually estimated by mixing the clay with various proportions of sand or other non-plastic material and determining the tensile, compression and transverse strengths of the mixture either in the plastic or dry state. The choice of a non-plastic material must depend on the purpose of the investigation; a right selection is very important, as a material may show a higher strength with one kind of sand than with another, or different results with the same sand ground or screened to different degrees of fineness.

The binding power is an extremely important property of plastic clays, as it affords a simple and excellent means of reducing their shrinkage on drying and

¹ *Int. Mitt. Bodenk.*, 1, 7-9, 10-43, 1911.

heating to within convenient limits and enables many mixtures having very desirable properties to be prepared with a facility which would otherwise be impossible. Binding power is often confused with 'plasticity', though the two properties are quite distinct, and some plastic materials are seriously deficient in binding power. The chief connection between the two is that when a material possessing binding power is mixed with a non-binding material the mixture may be plastic. Thus, a mixture of linseed oil and whiting in suitable proportions produces a plastic mass (putty), but neither the oil nor the whiting are individually plastic. The oil has, however, a considerable binding power. Unless the proportion of oil is excessive, the plastic mass of putty will differ from a clay of equal plasticity in being almost devoid of binding power.

The mechanism of the binding power of clays is discussed more fully in Chapter VIII.

Adhesion is the power whereby two masses remain in contact with each other and resist efforts to separate them. It is a complex property, the precise nature of which is imperfectly understood. It appears to involve surface tension and sometimes adsorption, as well as other factors.

The variable adhesion of clay to other substances is largely effected by their adsorption; if a little oil is applied to the surface so that no adsorption of the water in the clay can occur, the clay will not adhere.

The **adhesion limit** is reached when a mass of plastic paste ceases to adhere to other objects, such as the fingers. It forms one of the limits in the working of pastes, and is sometimes known as the 'sticky point'. The adhesion of clay to a metal surface is usually measured by the force necessary to detach a counterpoised metal plate from its contact with the clay surface.

Typical results are given in Table XIII.I.

Berridge¹ has found that when the $\frac{\text{volume of water}}{\text{volume of clay}}$ does not exceed 0.75, the angle of sliding is 45–60 degrees, but if insufficient water is present to appear at the surface, the clay will adhere strongly to wood, steel, and other metals. This adhesion may be prevented by introducing a film of water between the clay and the other surface—as by wetting slides for loading into ships or spades used in digging.

Lumps of dry clay show no adhesion so long as they remain dry, but a shower of rain, by wetting the surface, may cause the whole mass to slide.

Brittleness is a term used to denote the property of breaking quickly when a mass or article is subjected to a sharp blow or to a sudden shock. It is due to a lack of sufficient cohesion of the particles and to some extent to the hardness of the material, which prevents it from yielding under sudden stress and so causes it to break. For this reason, a very soft material is never brittle. Brittleness is generally a very undesirable property in ceramic materials. Burned ceramic materials which are brittle have usually been fired at too high a temperature, but some under-burned bricks are brittle if the vitrification has not been carried sufficiently far to bind the particles into a hard strong mass.

Brittleness may also be caused by cooling articles too rapidly, this treatment

¹ *Engineering*, 192, 1931.

producing a large number of minute cracks which render the articles weak. Brittleness may also be caused by using a kiln with a damp foundation. Some articles are brittle because crystals have formed in them during the burning or cooling period and some ceramic materials are brittle when heated on account of their large coefficient of expansion; thus, silica, magnesia, and bauxite bricks are very liable to crack and spall when heated quickly on account of the volume changes which occur during rapid heating and cooling. When heated for a long period, fused silica tends to become brittle on account of its recrystallisation or devitrification.

TABLE XIII—I

	<i>Cohesion when dry Grey clay being 100</i>	<i>Adhesion to iron plate 1 ft. sq.</i>	<i>Water in clay lbs. per c. ft.</i>
		lb.	
Sand	0·0	3·8	27·3
Humus	8·7	8·8	50·1
Sandy clay	57·3	7·9	38·8
Loamy clay	68·8	10·6	41·4
Brick earth	83·3	17·2	45·4
Grey clay	100·0	27·0	48·3

There is no reliable means of measuring brittleness; the best available is to investigate the effect of blows, applied in various ways, on the material (see 'Impact Tests' near the end of the present chapter).

Friability is the property which enables a material to break down readily when subjected to a crushing or abrasive force (p. 800). It is a typical characteristic of dry, sandy loams and of the soft, sandy bricks known as 'rubbers' which are largely used in decorative architecture, particularly in the south of England. These bricks are so rich in sand that they have little cohesion and when two of them are rubbed together they are rapidly 'worn away'. Most dry clays are very friable, but they lose this characteristic when heated to redness. Clays which, when dry, cannot easily be crushed or 'rubbed away' are known as 'indurated' or hardened clays; many shales, fireclays, and slates are indurated clays.

Malleability is the property which enables a material to change its shape without breaking or cracking when it is passed between a pair of rollers, or is subjected to a series of blows from a hammer or similar appliance. It is especially evident in such metals as gold, silver, and copper, but is equally characteristic of plastic clays and other pastes, though as these materials are soft it is not necessary to 'hammer' them. Malleability is due to the structure of the material being such that the particles can roll over each other without losing contact. It is an important characteristic of most ceramic pastes, but is usually referred to as 'plasticity'.

Ductility is the property which enables a material to be drawn or pulled into any shape; it also enables a material to be extruded through a small aperture at the end of the vessel containing it. This property enables bricks, pipes, and other articles to be extruded through a 'mouthpiece' attached to the end of a pugmill, 'stupid' or pipe-press, the extruded material being afterwards cut into pieces of suitable length by means of taut wires on a frame. Articles so produced are said to be made by the

'wire-cut' process. Although ceramic pastes are conveniently treated by this means, they are not nearly so extensible as some metals, such as gold, silver, copper.

The **workability** of a clay-paste is usually judged empirically by the 'feel', but it has been defined mathematically by Hind¹ as a constant (P) in the equation:

$$(M - M_0) = P \sqrt{\frac{E}{L}}$$

where M is the actual moisture content, M_0 a constant which is also the minimum moisture content, and E the extensibility of the clay for the length L (see *Plasticity*).

The ductility of clays and allied materials is usually regarded as part of their 'plasticity' (see Chapter VIII). This term has also been employed by Norton² to describe one aspect of the plasticity of clay masses (see also p. 484).

Extensibility is closely related to ductility ($q.v.$) and is expressed by the greatest increase in length which can be obtained in a mass without fracturing it. The extensibility is usually determined by measuring the distance between two points or fine lines marked on a test-piece made of the material, then applying a sufficient tensile force to break the material; the two pieces are carefully fitted together and the increase in length between the two marks previously made is noted. The result may be conveniently expressed as a percentage of the original length of the test-piece. In order that the results may be comparable, all the test-pieces should be of the same shape and size. A cylindrical rod, about 9 in. long with a diameter of 1.128 in. and, therefore, a cross-sectional area of exactly 1 sq. in., is convenient. The ends may be enlarged to facilitate the test-piece being firmly held in the tensile machine. The 'dots' or lines used as fiducial marks may be 4 in. apart. Sometimes the extensibility is measured on the test-piece used for determining the tensile strength, but it is often more convenient to use a longer test-piece and to apply the tensile force more slowly than when making determinations of the tensile strength.

The extensibility of a ceramic material is seldom determined, as such materials are seldom used under tension. It is chiefly of value in determining the plasticity of a paste by Zschokke's method (see Chapter VIII), as this investigator regards plasticity as measurable by the product of the extensibility and the tensile strength of the material.

Elasticity is the property which enables a material, after being drawn out or bent, to assume its original shape as soon as the flexile or tensile force is removed. The extent of deformation possible under these conditions is limited with each material, and when a greater force is applied, the material may either retain the distorted shape or it will break.

All pastes composed of plastic clay possess elasticity and increase in size when the pressure is released. The elasticity varies less with the water content than with the pressure and the material. The elasticity of clay pastes is usually greatest with a pressure of about 1120 lb. per sq. in., or 72 tons per sq. ft.

The elasticity of plastic clay is commonly ignored, but allowances must be made for it when making bricks or other articles by the wire-cut or extrusion process. The outlet of the machine must be a trifle smaller than the desired size of the articles

¹ *Trans. Brit. Ceram. Soc.*, 29, 202, 208, 1930.

Norton, F. H., *J. Amer. Ceram. Soc.*, 31, 236, 1948.

because, when the clay escapes from the machine, the elasticity of the clay causes it to increase slightly in volume. The more plastic the clay the greater its elasticity.

Flexibility is that property which enables a material to be bent without breaking it. Plastic clays and ceramic pastes possess a moderate degree of flexibility (otherwise 'handles' could not be made by bending a roll of paste), but this property is generally regarded as part of the 'plasticity' (Chapter VIII). Fired ceramic materials are seldom flexible, except to a small extent when at a high temperature near their softening point. *Torsional flexibility*, even to a minor extent, is desirable in some electrical insulators made of porcelain or stoneware, but under ordinary circumstances the flexibility of fired ceramic wares is neglected.

Toughness is the property which enables a material to resist tensile, crushing, and other disruptive forces. It is difficult to represent it by any single figure or test, as it depends on a variety of factors, the importance of which differ on different occasions. Thus, under some conditions, toughness may be synonymous with flexibility, under others with tensile or crushing strength or, in the case of some materials at high temperatures, it may be due to the viscosity of the semi-molten binding agent.

It is usually at a maximum in materials which have great cohesion, together with some flexibility or elasticity, and at a minimum in rigid materials, as the latter are liable to be brittle (p. 752). Toughness is commonly, but inaccurately, measured by the 'Rattler test' (p. 800), which chiefly measures the resistance to abrasion, though a hard material of a brittle nature which is not easily abraded will give a low result in the Rattler test, thus showing that toughness, or its converse brittleness, does affect the results of that test. Toughness may be regarded as due to a combination of (a) resistance to being drawn out, and thus is the converse of ductility; (b) resistance to flexion and torsion, and thus is the converse of flexibility; and (c) resistance to impact, and thus is the converse of brittleness. It is also related to hardness and viscosity. A property which is related to so many others is highly complex in its nature and almost defies definition or measurement.

According to L. Ogden¹ the toughness of porcelain is increased by increasing the proportion of flint and decreasing that of the felspar, whilst the proportion of clay is kept constant, or alternatively, if the proportion of felspar is kept constant, an increase in the proportion of flint and a decrease in that of clay will increase the toughness. Hence, the toughness of porcelain is dependent on the proportion of flint present, the strongest porcelains containing about 35 per cent.

Deformability is the property which enables the shape of a mass to be altered by the application of a force or combination of forces. It is not a simple property and cannot be determined as such, but is the converse of the transverse, impact, and torsional strengths of the material, and varies according to the means used for deforming the mass.

H. and F. Le Chatelier² found that substances may undergo successively three types of deformation: (a) elastic deformation, which is entirely removed when the deforming force is released; (b) a sub-permanent deformation, which disappears gradually after the removal of the deforming force; and (c) a viscous deformation, which does not disappear when the deforming force is removed.

¹ *Trans. Amer. Ceram. Soc.*, 13, 395, 1911.

² *Comptes Rendus*, 171, 695-9, 1920.

The deformability of a material is best estimated from a comparison of the effect on it of the various forces just mentioned.

Strength is a property which is expressed in several ways, of which the more important are:

1. *Compression strength* or resistance to compression: it is often known as the *crushing strength*.

2. *Tensile strength* or resistance to a 'pulling' force which tends to drag the particles apart.

3. *Transverse strength*—often termed the *modulus of rupture*, in which pressure is applied to the top of a long and rather narrow test piece which rests on two supports a pre-arranged distance apart.

Ceramic articles may be arranged in groups each having the same crushing strength or the same tensile strength, but these groups will not be identical as one sample may have a high crushing strength and a low transverse strength and another one may have a high tensile strength and a low transverse strength. There is no strict correlation between these various 'strengths'.

The strength of ceramic materials and articles at all stages of manufacture depends on (i) the structure or *fabric*; (ii) the chemical composition and the changes which have taken place or will take place at a later stage in production; and (iii) on any previous treatment to which the material may have been subjected.

A fibrous or matted material with or without a glassy or slag matrix forms the strongest product and is typified by the *true porcelain*s. Particles united by a glassy matrix or bond, as by a cement, depend for their strength largely on the strength of the individual particles or on that of the glass, but if correct conclusions are to be reached due consideration must be paid to the kind of strength determined. For instance, in the cold, the strength is best measured by a compression test, but at high temperatures a tensile strength test will more clearly reveal the weakness caused by the glassy matter as it becomes increasingly liquid.

The sizes and proportions of the various particles (including the proportion and nature of those in the colloidal state), the proportions of plastic and non-plastic materials and of water present all affect the strength in various ways.

The **crushing strength** of a material is the resistance which it offers to compression. It is often of great importance and is the kind of strength which is chiefly desired in most ceramic materials, especially those which in the fired state are used for constructional purposes, as they are often required to withstand a considerable pressure exerted by the materials above them. In order that a ceramic material may have a high crushing or compressive strength, (a) it must have a good binding agent which is present in sufficient amount to bind the particles of aggregate together; (b) the grains must interlock sufficiently, especially if the proportion of bond is small; and (c) the individual grains of aggregate must have great density and crushing strength, as porous particles are usually weaker. The crushing strength is, therefore, closely related to the texture of a material. These factors are considered more fully on p. 762.

Clays and other materials in a soft, plastic state show no end point when subjected to compression between two opposing plates, the sides of the sample being quite free, so that such materials have no definite crushing strength. When *in situ*

the bearing strength of a clay foundation is usually 2-5 tons per sq. ft., but this depends on the proportion of water present. When there is sufficient water, the bearing strength is reduced to zero.

The crushing strength of dried materials appears to be very variable (that of some air-dried clays is 1350 lb. per sq. ft.), but it is an advantage to know it when the materials or articles are to be piled on top of one another in a store, dryer, or kiln, as it is then possible to avoid spoiling them by piling them too high.

The compression or crushing strength of fired materials is often an important factor as regards their suitability for their intended purpose. In many cases the crushing strength of the cold material is of small interest, but that of the material at the highest temperature at which it is likely to be used may make all the difference as to its suitability for some purposes (see p. 775).

In addition to its direct use, the crushing strength of a ceramic material is also an indication of the uniformity of the heat-treatment to which the material has been subjected in the burning or firing process. If several pieces made of the same material and in the same manner are found to vary greatly in their resistance to compression, it may usually be concluded that the temperature in various parts of the kiln is far from uniform, those parts being the hottest which produce the strongest samples. The determination of the crushing strength requires a powerful machine (p. 791); for many purposes, a determination of the modulus of rupture or transverse test (p. 792) is equally satisfactory and is easier to execute in the absence of a crushing machine.

According to H. Le Chatelier and B. Bogitch, the modified Brinell test may be used as a substitute for the crushing test as the results are comparable, whilst the Brinell machine has the advantage of being more rapid, accurate, portable, and cheaper to use than a crushing press.

There is a sense in which the crushing strength of a ceramic material is definitely related to its physical rather than to its chemical properties. In other words it conforms to the general Mariotte-Boyle law that

$$pv = c$$

where p and v are suitably selected variables, and c a constant. If p (the pressure corresponding to the crushing strength) is taken as one variable, v may be a variable dependent on any other suitable property, such as density, porosity, or volume, and then

$$p = \frac{c}{v}$$

Griffith¹ has plotted the crushing strengths against the porosity (water absorption) of a very large number of ceramic articles and has found that the characteristic curve is a smooth one accurately conforming to the above expression, though he prefers to split the denominator into two parts making:

$$p = \frac{cs}{A + A_0}(1 \pm e)$$

¹ Griffith, J. H., *J. Amer. Ceram. Soc.*, 14, 325, 1931.

where p is the crushing strength in lb. per sq. in., c the efficiency factor, s the parameter or factor of dimensional stress, A the porosity (expressed as weight of water absorbed), A_0 another parameter which includes sealed pore-space, and e the probable error for a single datum. The working equivalent based on the tests is

$$p = \frac{80,000}{A + 4}(1 \pm 0.25)$$

This is equivalent to saying that the strength of a ceramic mass is determined solely by its density, and if a brick were wholly non-porous, so that $A + A_0 = 0$, the crushing strength would be 20,000 lb. per sq. in., or 1,285 tons per sq. ft.

The **tensile strength** is the resistance to a pulling force which tends to *extend* the material in the direction of the pull. It is also defined as the smallest tensile stress which will break the test piece into two pieces, and is found by dividing such stress by the cross sectional area at the centre of the cross-piece before the stress is applied. The result is expressed as lb. per sq. in. or kg./cm.² (see also p. 794).

The **transverse strength** or **modulus of rupture** of ceramic materials is often of great importance and, as it may be determined with very simple apparatus, determinations of it are increasing in popularity. It appears to be closely related in many ways to the crushing strength, though the two are by no means identical. The crushing strength is the resistance offered by a material to a given pressure; the transverse or cross-breaking strength is the resistance offered by a piece of the material of unit cross-section area to a bending or cutting force.

The *modulus of rupture* is calculated from the transverse strength by means of the formula shown on p. 792. The transverse strength undoubtedly gives a better indication of the resistance of a material to compression than does its tensile strength, although the latter is, in many cases, closely related to it.

Comparative determinations of the transverse strength of materials in various stages of production are very useful in preventing losses during manufacture. Thus, I. E. Sproat¹ found that the loss of biscuit ware in a pottery decreased from 7 per cent to 3.5 per cent when the cross-breaking strength of the dry body-mixture was increased from 200 to 300 lb. per sq. in. They are also useful in comparing the strengths of slabs, tiles, thin paving bricks, pottery, saggars, etc., in order to increase their durability.

According to Bleining and Howat, the transverse test of a dry mixture of clay and sand is a better indication of its plasticity than the tensile or compression tests. It is, however, unwise to place much reliance on the assumed relationship of any 'strength test' of a dry material with its plasticity.

A comparison of the transverse strength of saggars and other hollow-ware, subject to irregularly distributed loads, often enables articles of a better quality to be produced.

In considering these various kinds of 'strength', it will be seen that for most purposes an article of ceramic material must possess a combination of two or more of these qualities, the ones required depending on the purpose for which the article or material is to be used. Thus, the plastic raw paste used for making articles must

¹ *J. Amer. Ceram. Soc.*, 5, 588, 1922.

be readily deformed or shaped and must, therefore, have a low cohesion so as to allow the particles in the paste to move relative to each other, and yet the material must possess ductility and malleability (or plasticity), together with sufficient tensile, compressive and transverse strength to prevent fracture when the shape of the mass is altered. On the other hand, a finished article must usually have a high degree of cohesion to enable it to retain its shape under the conditions to which it is likely to be subjected, and it should also possess such properties as toughness and should not be brittle.

FACTORS AFFECTING STRENGTH

MANY factors affect the strength of ceramic materials, the most important of which may be grouped under the following heads:

- (a) The chemical or mineralogical composition of the material.
- (b) The physical properties of the material.
- (c) The mode of preparation of the material.
- (d) The mode of manufacture of the article.
- (e) The conditions of drying.
- (f) The conditions of burning.
- (g) The temperature at which the article or material is used, or at which its strength is determined.
- (h) Other conditions to which the article or material is or has been subjected, including weathering, sudden changes of temperature, prolonged heating, etc.

The strength of raw clay will depend chiefly on factors (a), (b), and (h), and chiefly on the second; the strength of a dried clay will depend on factors (a) to (e); the strength of freshly-burned products on (a) to (g); whilst the strength of articles which have been in use for some time may be further complicated.

In order to ascertain the effect of these various factors upon the strength of ceramic materials they should first be studied separately, and afterwards in combination.

The **Chemical or Mineralogical Composition** frequently has a very important effect on the strength of ceramic articles, but care must be taken not to exaggerate its influence; in the past there has been a tendency to attach undue importance to the chemical composition and to neglect the physical characteristics of the materials.

The chemical composition of the raw or dried materials is of less importance, than in fired products, as in such materials chemical reactions take place very slowly, if at all, at ordinary room temperatures. When the materials or articles made of them are heated to such a temperature that chemical reactions can take place, the chemical composition of the material begins to play an important part.

The strengths of raw and dried clays and the factors which influence them have been described in Chapter VIII (see also p. 781).

Most finished articles made of ceramic materials consist of solid particles of 'aggregate' united by a glassy bond, the nature of the latter largely determining the strength of the article at various temperatures. As the bond is usually produced by the combination of the binding agent with some of the constituents of the aggregate,

the strength of the mass also depends on the amount of bond present and on the total proportion of fluxes which are present in the raw materials. In a cold ceramic mass, the greatest strength will usually be found in the material containing the largest proportion of fluxes, such as soda, potash, lime, magnesia, etc., provided the ware has been fired at a sufficiently high temperature to render the fluxes effective. At high temperatures, on the contrary, the larger the proportion of fluxes, the lower will be the strength of the mass, because at a high temperature the bond produced by the fluxes will be soft and mobile and, therefore, unable to impart the necessary rigidity to the material. When the temperature is reduced sufficiently for the molten glassy matter to become solid, the strength of the material as a whole will greatly increase as the solid glassy matter forms a strong bond.

The effect of the chemical composition on the strength of a ceramic material is shown in the case of bricks made of *lime*; these are extremely weak, as no suitable bond can be found for them. Other non-plastic materials, such as bauxite, when attempts are made to shape them without an added bond, are very weak, but if a suitable bond, such as clay or lime is used, very strong bricks and other articles can be made, some bricks bonded with lime having a crushing strength of 10,000 lb. per sq. in. Some magnesia bricks (especially those containing about 5 per cent of ferric oxide or its equivalent) are very strong when cold. On the other hand, some silica bricks are weak because of the poor quality and small proportion of lime used in making them.

Articles made of clay owe their strength when in the moist and dry states chiefly to the plastic material present, but in the fired or burned articles the plasticity is destroyed and the strength of the articles is then largely dependent on the proportion of active fluxes present. These fluxes combine with the free silica present and form glossy molten silicates. Blue bricks and other similar vitrified articles contain a larger proportion of active flux than red bricks and are, consequently, stronger. Blue bricks, tiles, etc., are particularly interesting in this respect, as the amount of glassy bonding material is not due so much to the total metallic oxides present, as to the fact that the chief of these oxides (iron) is reduced to the ferrous state by the mode of burning adopted and so is converted into an active flux. Under oxidising conditions it is largely inactive.

The effect of fluxes on the transverse strength of terra-cotta is shown in Table XIII.II, due to E. C. Hill.¹

Fireclay bricks increase in strength in the cold with an increase in the proportion of fluxes, but, as previously mentioned, their strength at high temperatures is lessened by the addition of fluxes or of free silica (sand).

As would be expected, the higher the temperature of firing, the greater will be the proportion of liquid produced. This liquid which is responsible for the low strength at high temperatures, solidifies to a glass on cooling, thereby producing a vitrified mass of great retentive power when measured in the cold. In general the amount of liquid produced at the temperature of firing will be in proportion to the cold strength, hence it follows that an alumina-rich fireclay will not have so high a crushing strength as one with a greater content of silica provided that both are fired to the same temperature and that they have been prepared in the same way.

¹ *J. Amer. Ceram. Soc.*, 5, 832, 1922.

The presence of free silica as quartz, tridymite or cristobalite in the fired brick reduces the strength in a marked fashion. This is particularly true of low-grade fireclays and clays used in the manufacture of common bricks. Quartz is not readily attacked by the other components of clays when heated up to 1250° C., hence it does not enter into the liquid phase.

TABLE XIII—II. EFFECT OF FLUXES ON THE STRENGTH OF TERRA-COTTA

	<i>Modulus of Rupture</i> lb. per sq. in.
Terra-cotta clay	1518
+ 5 per cent Maine felspar	1486
+10 " "	1905
+2.5 " Powdered glass	1489
+5.0 " " "	1687
+2.5 " White lead "	1372
+5.0 " " "	1461
+1.25 " Cryolite "	1339
+2.5 " " "	1426
+1.25 " Whiting	1618
+2.5 " " "	1503
+5.0 " " "	1545
+2.5 " Fluorspar	1275
+5.0 " " "	1326
+1.25 " Magnesium carbonate	1269
+2.5 " " "	1240
+5.0 " " "	1152
+5.0 " Furnace slag "	1361
+10.0 " " "	1407

Other substances, besides those commonly regarded as fluxes, may affect the strength of clays and refractory materials; in a complex chemical substance or mixture, such as those used for making fireclay goods, the respective proportions of the constituents is of great importance. Thus, the presence of an excess of bone ash in china ware increases the brittleness of the product.

The nature and the grain size of the constituent minerals in a clay may also influence the strength of the fired product both at high temperatures and in the cold. Micaceous components, for example, flux readily to form a liquid mass at low temperatures provided that the grain size is small. Larger particles, however, react much more slowly and may not appreciably alter the strength unless the firing has been prolonged.

The effect of chemical composition is considered in more detail in Chapter XI.

Within the last few years increasing interest has been shown in *chemical bonding* as a means of improving the strength of refractory and ceramic products. For instance, in making magnesite bricks and shapes with a high resistance to basic slag at high temperatures it is customary for the raw material (which may be the carbonate or the hydroxide) to be fired twice; the first firing (dead-burning) forms the stable oxide, periclase (MgO), by burning in a shaft or rotary kiln. This calcined material must then be crushed, graded and moulded to shape, followed by a further

firing to develop strength. This final burning can be avoided by adding a proportion of a magnesian cement, such as magnesium oxy-chloride, prior to moulding; the cement sets in contact with water and strength is imparted to the brick shape without further firing. It is claimed that bricks made in this way are three times as strong as those prepared by the double-firing process.

Sodium silicate has been used as a cement for ceramic materials for some time but it has the disadvantage of seriously reducing the refractoriness. Organic silicates are being used on an increasing scale, for these yield pure colloidal silica on calcination which is an efficient bond and does not unduly reduce the refractoriness.

The **physical properties** of ceramic materials have a very important influence on their strength. The chief physical properties to be considered are (a) the size and shape of the article; (b) the texture of the material; (c) the porosity; (d) the coefficients of expansion or contraction; and (e) the adhesive power of the bond.

Size and Shape. The crushing strength is to some extent dependent on the size of an article or mass, and usually the larger an article the greater will be the total power required to crush it, though it need not necessarily have a high crushing strength, as the latter is expressed in terms of unit area (lb. per sq. in.). The shape has an important effect on its strength, for if it is designed badly it may be unduly weak in certain parts and so bend or crack when subjected to a great stress. For instance, sharp corners and sudden changes in the thickness of an article are sources of weakness, and, where possible, these should be avoided. The apparently abnormally great strength of hollow columns as compared with solid ones is well known and it is worthy of note that perforated bricks are stronger in proportion to their area than solid ones, as shown in Table XIII.III, due to Professor Tetmaier.¹

TABLE XIII—III. PERFORATED *v.* SOLID BRICKS

<i>Crushing Strength, tons per sq. ft.</i>		<i>No. of Holes</i>	<i>Diameter of Holes in.</i>
<i>Solid Bricks</i>	<i>Perforated Bricks</i>		
276	411	14	0.6
161	178	12	0.7
147	149	12	1.0
130	154	10	0.7
202	238	14	0.8
329	383	14	0.8

Seeger also found that a solid and a perforated brick made from the same material had crushing strengths of 315 and 504 tons per sq. ft. respectively.

Texture is concerned with (a) the shapes and sizes of the individual particles, and (b) the arrangement and size of the pores or interstices between the grains. In ceramic materials, the maximum strength is obtained by the use of irregular, angular grains of numerous sizes, which interlock freely; rounded grains produce a weak mass as they cannot interlock properly. Thus, bricks made of powdered calcined flint or of sea-sand are usually weak, because the grains are rounded and, consequently, do not hold well together. The strength of a ceramic mass, both in the

¹ *Brit. Clayworker*, 29, XXII, 1920-21.

dried and fired state, usually increases with the fineness of the grains, but an excessive proportion of fine grains is undesirable.

One of the most important factors which influences the green and dry strength of raw clays is the specific surface area or surface area per unit weight of material. This aspect has been studied by T. E. Currie¹ who found that the dry strength of a wide variety of kaolin-type clays was related to the available surface area. Some results are shown in Table XIII.IV.

TABLE XIII—IV. THE RELATION BETWEEN THE
TRANSVERSE STRENGTH AND THE SURFACE AREA OF
SOME KAOLIN-TYPE CLAYS

<i>Clay</i>	<i>Transverse Strength (gm./sq. cm.)</i>	<i>Specific Surface Area per 100 gm. of clay</i>
Bond clay	1140	11.64
Devon ballclay	805	9.20
Dorset ballclay	660	7.15
Scottish fireclay	480	1.81
Stourbridge fireclay	440	1.78
Yorkshire fireclay	650	2.57
Durham fireclay	385	1.17
Shropshire fireclay	435	1.67

The relationship between dry strength and surface area is approximately logarithmic and of the form:

$$\log S = aA + b$$

where S is the cross-breaking strength of the dried material, A is the surface area per gram of clay and a and b are constants.

The presence of small particles facilitates reactions on firing and is the probable reason for the increase in strength when such material is present. With too many fine particles, excessive shrinkage may occur and then warping, distortion and loss of strength will certainly result.

The addition of sand, grog, or other material to reduce the shrinkage and facilitate drying, lessens the hardness of the fired articles unless the heating is sufficient to cause partial vitrification.

In addition to angular grains, some ceramic products (particularly porcelains and some refractory wares) contain a felted mass of crystals of mullite. This is probably the reason why porcelains rich in mullite are superior to others in mechanical strength and in resistance to thermal shock. The size of the grains of grog in fireclay mixtures has an important influence on the resistance of the fired material to transverse loads at high temperatures. Large ceramic slabs or other articles which are required to carry heavy loads should be made of comparatively coarse material. Various investigators are agreed that about 50 per cent of grog sizes corresponding to 4–20-mesh should be used and all fine materials should previously have been removed from it. This is also recognised in the Standard Specification for Retort Material, etc.

¹ Currie, T. E., B.Sc. thesis, Leeds Univ., 1951.

The strongest unfired mass consists of a suitably graded mixture of angular grains of various sizes selected so as to produce as compact a mass as possible and provided with a sufficient amount of binding material to cover each particle of aggregate and to unite them together. The production of graded aggregates of this kind is described on p. 373. The proper interlocking of the particles of aggregate is of very great importance, and the low transverse strength of many fireclay and other slabs is due to their being made of badly-graded mixtures. Similarly, the strongest burned material consists of a mass of interlocking crystals formed *in situ* and united by a glassy cement. Such a mass is stronger and more compact than can be obtained by any artificial means of assembling the particles.

It should be observed that the texture of a mass is not always uniform in every direction on account of the method used in shaping it. Thus, if a tile is made by applying pressure to its upper and lower surfaces, its structure when laid flat will not be quite the same as that when it is on edge. Hence, in all machine-made products, and to some extent with hand-made ones, the structure varies in different directions, and this should be taken into consideration when investigating the strength of an article.

Further information on texture will be found on p. 367.

Porosity. The size and arrangement of the pores in a ceramic mass affect its strength, inasmuch as the larger and more numerous are the pores, the thinner must be the enclosing 'walls' of solid material. Hence, a highly porous material—if the pores are large—must be weak. When the pores are extremely small, their effect on the strength of the material is less noticeable.

In many fired ceramic materials, the tensile and crushing strengths are roughly inversely proportional to the porosity. Thus, if certain bricks having a porosity of 6–12 per cent have a crushing strength of 7000–15,000 lb. per sq. in., other bricks of a similar character, but with a porosity of 14–25 per cent, will probably have little more than half the strength of the former ones.

In ceramic materials, it appears that great strength is incompatible with high porosity, though there is only a very indefinite relation between the porosity and strength of such materials.

Power of the Bond. In ceramic materials five types of bond occur: (a) bonds of a plastic nature, such as clays; (b) bonds of an adhesive nature, such as glue, dextrin, molasses, etc.; (c) bonds of a hydraulic nature, such as mortar and Portland cement; (d) glassy bonds such as occur in vitrified ware; and (e) crystalline bonds where the body is held together by a felted mass of intergrowing and interlocking crystals.

Each of these bonds increases the strength of the mass as a whole, though to very different extents and in very different ways (see also Chapter VII).

A *plastic agent*, such as clay, possesses a peculiar binding power (p. 782), whereby it is able to extend its plastic properties to limited proportions of non-plastic materials which may be mixed with it, and when the mixture is dried and afterwards burned, the mass becomes stronger than before, although it has lost its plasticity.

Shales and indurated clays produce masses which are weaker in the raw and dried state, but develop great strength on firing, so that the strength finally attained may not be greatly different from that reached by more plastic clays and non-plastic

material. The chief difference in this respect is that whilst plastic clays will develop great strength when heated to a relatively low temperature (900° – 1000° C.), lean clays must be heated to a higher temperature (1200° – 1600° C.), so that they undergo considerable vitrification in order to attain the same strength.

An *adhesive*, such as glue, tar, viscous mucilage, dextrin, flour or starch paste, heavy mineral oils, cellulose or molasses, forms a coating around each of the particles and so unites them together. The resultant mass will be moderately strong when dry, but as such adhesives are destroyed by heat they can only be used to a limited extent in connection with ceramic materials. When non-plastic material is to be made into bricks an adhesive is often added to confer strength prior to firing. After such treatment, the dried mass will be strong enough to handle and stack and although there will be a rapid reduction in tenacity when the gum begins to burn away, provided the setting has been carefully carried out there should be no collapse.

Cellulose sulphite lye and molasses are common adhesives in refractory practice the former being of particular value in silica and basic production. Although adhesive bonds are burnt away at moderate temperatures, they leave no residue and, for this reason, are preferred to clay bonds which alter the chemical composition of the product.

A *hydraulic bond*, such as Portland cement, lime, etc., behaves like an adhesive, so far as the dried materials are concerned. On heating the mixture, the hydraulic bond is usually converted into a glassy bond.

A *glassy or vitrified bond* consists of a glass- or slag-like mass of molten material which, when the ceramic material containing it is at a sufficiently high temperature, melts and flows into the interstices between the solid particles. At that stage the mass as a whole is weak, but when it has cooled and the bond is solidified, an extremely strong bond is obtained. A glassy bond can seldom be used when the material is in the moist or dried state—unless water-glass (a sodium silicate) is included in this type of bond—as it only becomes adherent when fused and afterwards allowed to solidify.

In most ceramic materials, the glassy bond is produced when the articles are in the kiln and, consequently, such materials only attain their maximum strength after they have been 'burned' or 'fired'.

A *crystalline bond* is, as the name implies, one in which the body is essentially composed of crystals which grow together; the best analogy is a box of pins, although a better representation would be given if each join or point of contact between the pins were welded.

The best conditions for crystalline bonding are when needle-shaped crystals are produced in large quantities at the temperature of firing. Thus the development of mullite in aluminosilicate mixtures may give rise to a felted mass of acicular crystals.

In general a crystalline-bonded material is not as strong in the cold as one which is essentially glassy, but in the former the strength is maintained virtually unchanged until the crystals themselves melt. Thus, mullite brick, free from any glass, will suffer little change in shape under a load up to about 1750° C.

The **mode of preparation** of ceramic materials often has a very important influence on the strength of articles made from them.

The *grinding* of the materials determines the sizes and shapes of the various particles and so directly affects the strength of the mass (p. 762).

The *amount of water* present or added to the material largely influences the strength of the mass, both directly in the damp material and indirectly in the dried and fired product.

When less water is present in the ground raw material than will form a thin film around each particle, the addition of a further quantity of water will increase the strength of the material. When each particle is completely surrounded by a film of water of the required thickness, the addition of further water will effect a reduction in the strength and an increase in the fluidity of the mass.

TABLE XIII—V. EFFECT OF AMOUNT OF WATER ON STRENGTH

<i>Water, per cent</i>	<i>Compressive Strength after drying kg. per sq. cm.</i>	<i>Compressive Strength after burning at 1300° C., kg. per sq. cm.</i>
15	12	180
16	13	195
17	15	190
18	15	220
19	17	250
20	19	265
21	20	270

A deficiency of water is usually preferable to an excess in the preparation of ceramic materials.

The effect of using a variable proportion of water in the manufacture of silica bricks containing $1\frac{1}{2}$ per cent of lime, the whole material being ground to 200-mesh, is shown in Table XIII.V, due to M. Philippon.¹

Further information on the effect of water will be found in Chapter VIII.

The *proportion of added materials*, such as the bonding agent, etc., may seriously affect the strength of the prepared material.

Sometimes a very small proportion of an added material will have a very marked effect on the strength of the product. This is particularly noticeable in the case of *electrolytes*, which, when added to clay in the form of pastes and slips, considerably increase the strength of some dry and fired goods made from them, though few figures have been published which show the actual increase.

The mechanism by which the strength of materials is increased by the addition of electrolytes is probably intimately linked to the deflocculating effects described in Chapter VIII. Colloidal particles are more readily dispersed in water when electrolytes are present and a better distribution of plastic material is thereby achieved.

H. W. Douda² has found that the addition of 1 per cent of sodium hydroxide increased the dry strength of a stoneware clay by 79.22 per cent on the unground material, and nearly trebled it after wet grinding. A flint clay which showed a

¹ *Rev. de Métal.*, 15, 51, 1918.

² *J. Amer. Ceram. Soc.*, 3, 885, 1920.

modulus of rupture of 305 lb. per sq. in. after wet grinding with plain water, had its modulus of rupture increased to 439 lb. per sq. in. when the material was ground with a 1 per cent solution of sodium hydroxide.

The *method of mixing* ceramic materials has a very great influence on the strength of the products. If, as is often the case, the mixing is incomplete, the strength of the articles will vary in different parts of their structure. The process of 'pugging' is a far less effective method of mixing than 'tempering' the material in an edge-runner mill¹ with revolving pan (the so-called wet-pan mill), though pugging is much cheaper than tempering. H. W. Douda² has found that by tempering a stone-ware clay for two hours in a wet-pan mill, he increased its strength by 74 per cent

TABLE XIII—VI. EFFECT OF TEMPERING
ON STRENGTH OF SILICA BRICKS

<i>Time of Tempering mins.</i>	<i>Modulus of Rupture lb. per sq. in.</i>
10	440
15	446
20	499

when dry and doubled its strength when burned at Cone 2. Similarly, the modulus of rupture of a dried flint clay was raised from 35 lb. per sq. in. to 305 lb. per sq. in. after tempering the wet material for two hours in a wet-pan mill. Similar increases in the strength of the dried goods were obtained with several different materials.

The *time* occupied by the mixing or tempering process also has an important effect on the strength of the product. Not only is a sufficient period of mixing or tempering very necessary to secure a uniform mixture of the materials, but it will also be found that imperfectly mixed ceramic materials are a constant source of annoyance and loss. On this subject, also, little information has been published respecting clay wares, but Table XIII.VI, due to R. M. Howe and W. R. Kerr,³ shows the effect of the time of tempering on the strength of silica bricks.

The difference is much greater with clays than with non-plastic materials.

Ageing. When a plastic material has been mixed, its preparation is not finished; it should, if possible, be set aside for several days in order to 'age' it.

This 'ageing' of clay pastes has an important effect, as it appreciably increases the strength of the product, especially in the dry state, by securing a more even distribution of the water present and facilitating the retention of the colloidal matter in the mass. The period of rest during which the material is 'ageing' may vary from a few hours, which has an appreciable effect for some clays, to the period of a century or more, which is reputed to be the length of time which the ancient Chinese kept

¹ Care should be exercised during tempering to ensure that no reduction in particle-size occurs, otherwise the grading and other properties of the material may be drastically changed. This can be a serious disadvantage when using an edge-runner mill and for the best results, these machines should be operated with the rollers raised and an extra paddle or churn introduced.

² *J. Amer. Ceram. Soc.*, 3, 885, 1920.

³ *J. Amer. Ceram. Soc.*, 5, 164, 1922.

their pastes prior to using them for the manufacture of china and porcelain. It is seldom practicable to allow more than a fortnight for ageing brick and tile clay, but for much coarse pottery a shorter period may suffice. An adequate period for 'ageing' is almost essential to the production of retorts, glass-pots, and crucibles of best quality, as all these articles are required to withstand severe conditions when in use.

The effects of ageing are not so marked with non-argillaceous materials, though still apparent. For further information on 'ageing' see Chapter VIII.

Effect of Shaping on Strength. The method of shaping articles has an important influence on their strength. Hand-moulded articles are seldom as strong as machine-made ones, provided the machine is of a suitable character for the material. It is not always easy to ensure the suitability of the machinery, as so much depends on apparently trivial properties in the material. Thus, in making articles by extrusion or expression, a defective die or mouthpiece puts an excessive strain on the column of clay as it issues from the opening and so the material may crack. The cracks may not be serious and sometimes are not visible when the articles are in the freshly-made state, but during drying and firing, cracks or other defects may develop and seriously weaken the goods. A laminated structure is sometimes imparted to a column of clay made by extrusion; it is usually due to lack of sufficient space between the bridge which carries the knives of the machine and the end of the mouthpiece, but it may also be due to the lamellar structure of the original clay (p. 53).

The various methods of shaping ceramic articles afford many other opportunities for reducing the strength of the material. Thus, if they are shaped by compression in a press which does not apply a uniform pressure over the whole surface, the resulting article will be subject to internal strains and will have a low strength, no matter how great a pressure may be applied to some parts of it.

When the pressure is applied uniformly, its amount affects the strength of the product. Under normal conditions, the greater the pressure applied the greater will be the strength of the article produced. Thus, Table XIII.VII due to Watkin,¹ shows the effect of the pressure applied in producing tiles by compression of an almost dry clay-dust on their tensile strength.

An increase of moulding pressure has a pronounced effect on the strength of refractory bricks. Shapes made by dry press methods may be more than twice as strong as those which are wet moulded.

Although the appearance of bricks and tiles may be improved by double pressing, they may suffer a reduction in strength unless care is taken to ensure that a disturbance of the mass does not occur in the repress; if the box is too large a heterogeneous body may be formed.

Effect of Drying on Strength. The manner in which articles made of clay and allied materials are dried has a great influence on their strength when in the dry and also in the fired state. To avoid rupture, all materials having plastic or kindred properties must be dried under conditions which will permit the water to be removed at a uniform rate throughout the mass and without the formation of an impervious skin or crust through which water from the interior of the mass cannot penetrate. The necessity of drying under suitable conditions (see Chapter IX) is particularly

¹ *Trans. Eng. Ceram. Soc.*, 17, 111, 1917-18.

great with articles containing a large proportion of plastic clay, as these are specially liable to form a hard surface-skin which, at a later stage in the drying, is very liable to crack under the pressure of the water vapour which cannot escape through it. The partly-dried material is very weak and cannot withstand the strains produced in it by the pressure of water vapour in the interior and by the uneven contraction. Joints in the articles are usually very weak at this stage, and so need special care in drying, and also when drying articles which vary greatly in thickness in different parts. When articles are dried before being placed in the kiln it is often desirable not to remove the whole of the water, as this causes them to become very friable and difficult to handle without rubbing the edges and fine mouldings, and so causing irreparable damage. A very small proportion of water is sufficient to overcome this difficulty.

TABLE XIII—VII. EFFECT OF PRESSURE ON STRENGTH

<i>Pressure lb. per sq. in.</i>	<i>Tensile Strength lb. per sq. in.</i>	<i>Pressure lb. per sq. in.</i>	<i>Tensile Strength lb. per sq. in.</i>
4000	1400	2000	850
3750		1750	850
3500	980	1500	960
3250		1250	960
3000	1150	1000	940
2750	—	750	810
2500	1060	500	790
2250	1060		

Materials consisting largely of plastic clay increase in strength and rigidity when dried slowly and, under favourable conditions, the more thorough the drying the greater is the crushing strength. For this reason, an article which has been air-dried at ordinary room temperature may have only about half the strength of a similar one which has been dried at 100° C. The difference in strength is due to the small proportion of moisture still left in the air-dried product, which enables the material to retain some of its original mobility.

The effect of cooling the completely dried material in a desiccator so that it cannot absorb moisture from the air during cooling is appreciable.

The strength of wholly non-argillaceous materials increases to some extent during the drying, but when fully dry they are not usually so strong as articles containing clay, because they do not contain so much or so strong a bond. In most cases, such materials are much more porous than those containing clay, so that the moisture escapes more readily and the shrinkage is much less. There is, consequently, little liability of damage by rapid drying, as the strains which may occur in clay ware do not arise. For this reason, non-argillaceous materials may usually be dried quite satisfactorily at a fairly rapid rate.

Effect of Burning on Strength. The conditions to which ceramic articles are subjected in the kiln form one of the most important factors in determining their final strength. If they have been heated at a sufficiently slow rate, so as not to crack them,

they will be much stronger after firing than in the plastic or dry state, the final strength depending chiefly on (i) the nature and amount of the bonding material produced during the heating; (ii) the particles of aggregate united by the bond; and (iii) the better consolidation of the grains of material which results from the shrinkage of the material during the firing.

The *bond* affects the strength of the fired material after the latter has been allowed to cool, because the bond is, as its name implies, the agent which unites the other particles together. Consequently, the stronger the bond and the larger the proportion of it present, the stronger will be the articles. For this reason, vitrified masses—in which all interstices between the particles of aggregate are filled with the bond—are stronger than porous ones; the vitrified material not only contains a larger proportion of bond, which unites the other particles together more securely, but the bond itself also possesses great intrinsic strength. Clays containing at least 6 per cent of ferric oxide, or its equivalent, when fired in a reducing atmosphere, form a strong product, because the reduced iron oxide acts as a flux, combines with the clay and so produces a mobile fluid of fused matter which penetrates and fills the pores (see Chapter XI). When the same clays are fired in an oxidising atmosphere, the oxidised iron oxide does not fuse, and the small proportion of fused material formed does not fill the pores, so that a weaker and less vitrified article is produced. Porcelain, china, stoneware, and other articles of a vitrified nature are all much stronger than porous materials.

Refractory materials, in general, contain a much smaller proportion of glass than a vitrified ceramic product; consequently they are not as strong when tested in the cold, for their porosity is comparatively high. At elevated temperatures, however, refractory articles will retain their strength and suffer little deformation, because there is insufficient glass to liquefy. Glassy ceramic materials, on the other hand, melt and lose strength at much lower temperatures.

The *aggregate* affects the strength of an article according to the strength of the individual grains of which it is composed, unless these grains are porous and are completely saturated with the bond, in which case their strength may be increased.

The *shrinkage* which a material undergoes in firing affects its strength as described on p. 516, but if the shrinkage is excessive it may reduce the strength of the finished article on account of the large amount of rearrangement which the particles undergo during the heating and shrinking; this is particularly the case with mixtures which are heterogeneous in character and are deficient in vitrified bond. When a large amount of vitrification occurs, greater changes in the volume of the material may take place without decreasing the strength, though an excessive amount of vitrification must be avoided or deformation or cracks may result. The maximum strength in a fired mass is usually obtained when the amount of vitrified material or bond is just sufficient to fill the pores and to unite all the individual unfused particles, but there is not enough to separate these particles from each other to an extent which allows them to slide or slip apart. For further information on shrinkage see Chapter XII.

The *temperature attained in the firing* affects the strength of the finished and cold articles, because it determines, to a large extent, the amount of fusible matter or bond produced, and this, in turn, controls the strength of the mass. The effect on the

cold crushing strength of firing materials at various temperatures is shown in Table XIII.VIII, due to Saxe and Buckner:¹

TABLE XIII—VIII. EFFECT OF FIRING TEMPERATURE ON CRUSHING STRENGTH OF CLAY

Clay	Room Dry 20° C.	55° C.	110° C.	200° C.	325° C.	575° C.	825° C.
Ball clay	61	89	125	110	111	195	221
Ball clay	38	60	62	76	84	126	163
Ball clay	36	59	66	73	78	129	158
Plastic clay	89	114	134	129	133	151	468
Ball clay	61	80	94	98	103	151	266
Plastic clay	85	107	125	121	119	184	322
German crucible clay	86	91	114	127	141	253	331
American crucible clay	73	104	145	145	153	255	294
Slip clay	14	19	24	17	19	9	24
Slip clay	57	75	88	80	87	92	274

Grimshaw and Sutton have measured the effect of the firing temperature on a series of Pennsylvanian shale clays used for brick-making. The transverse strength increased in remarkable fashion with the development of a glassy phase as shown in Table XIII.IX.

TABLE XIII—IX. EFFECT OF FIRING TEMPERATURE ON THE COLD TRANSVERSE STRENGTH OF PENNSYLVANIAN SHALE CLAYS

Sample No.	Modulus of Rupture (lb. per sq. in.)									
	Room Temp.	110° C.	300° C.	500° C.	600° C.	700° C.	800° C.	900° C.	1000° C.	1100° C.
1	87.2	127.4	90.4	108.3	91.1	108.0	147.7	935.2	3,279	6,540
2	73.3	115.0	64.4	72.5	69.6	74.5	89.9	764.3	2,759	8,450
3	45.0	87.0	57.7	49.3	47.2	n.d.	58.8	332.5	1,469	4,708
4	91.6	170.9	106.1	109.2	119.7	128.9	170.2	1,400	6,379	bloat
5	102.9	146.2	100.1	98.6	102.8	110.9	123.4	1,212	2,533	6,164

The strength of clays which have been heated to points within the range 110° C. to 325° C. is practically constant, but then begins to increase as the temperature of firing is increased. At temperatures of between 400°–600° C. most clay minerals undergo decomposition and in this region a pronounced reduction in tenacity may occur, because of the loss of strength in the bonding material.

Above 1000° C. the amount of liquid formed increases considerably. On cooling, this liquid solidifies mainly to a glass which acts as a cement serving to bind the mass together, thereby conferring great strength on the body when tested at room temperatures.

¹ *J. Amer. Ceram. Soc.*, 1, 113, 1918.

The effect of liquid formation on the strength of clay products at high temperatures is shown by heating test pieces under the influence of a tensile stress to elevated temperatures. A gradual increase in length is observed until at a certain point the extension increases rapidly and eventually the test-piece breaks. A typical temperature-extension curve of fireclays is shown in Fig. XIII.2 in which the point A corresponds to a temperature of about 1500° C. If the tensile stress is not too large (under 550 gm. per sq. cm.) the resultant curve shows a slight contraction immediately before the rupture of the test-piece.

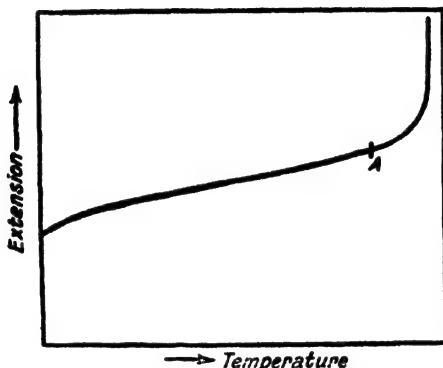


FIG. XIII.2. TYPICAL TEMPERATURE-EXTENSION CURVE FOR FIRECLAYS

The *creep*, or rate of extension when subjected to a tensile stress, of fireclays and glass-house pots has been measured by Partridge and Adams¹ at various temperatures at which the test-pieces were maintained for periods up to 100 hours. The time-extension curve is a characteristic part of a parabola until the point of rupture is reached when failure occurs quite suddenly. The authors concluded that glass-house pots made of siliceous clays show less creep than those of aluminous ones and that conditions of stress are more uniform; grog decreases the tensile strength of clayware at high temperatures.

The lack of strength in many bricks, saggars, etc., is due to the fact that insufficient care is taken in firing them. Some saggars, for example, are merely placed in a kiln with other goods and burned at the same rate as the latter, with the result that the temperature to which they are heated is not sufficiently high to produce the maximum attainable strength. If such saggars were fired independently to a higher temperature their strength would be considerably increased, though the cost of this additional firing must not be overlooked.

Das and Roberts² have studied the variations which occur in the rigidity of silica refractories when heated up to 1620° C. and subjected to torsional strain. A pronounced decrease in modulus was recorded in the region of the inversional changes of tridymite and cristobalite but the value increased rapidly above this

¹ Partridge and Adams, *J. Soc. Glass Tech.*, 15, 193, 1931.

² Das, S. S. and Roberts, A. L., *Trans. Brit. Ceram. Soc.*, 48, 215, 1949.

temperature up to about 1200° C. In certain cases, the rigidity attained a maximum which was five times greater than that recorded at the inversion temperatures. At still higher temperatures, the rigidity decreased slowly, but even at 1400° C., it tended to be greater than that at room temperature. No plastic flow was detected below 1400° C.

Wiechula and Roberts¹ carried out similar tests on a range of alumino-silicate refractories. They showed that where the material tested was rich in crystalline silica a marked increase in rigidity was recorded up to temperatures of about 700° C. When mullite or corundum was the dominant crystalline phase the change in rigidity was less or non-existent. In all the samples tested, a transition occurred between 700°-800° C. from complete rigidity to incipient plasticity irrespective of the composition of the material. The rate of 'flow' was less with material of high alumina content and the authors considered that this was related to the increase in the amount and probably the grain size of mullite and corundum crystals.

In general, the higher the temperature of firing the greater is the cold crushing strength of the products because the amount of glass and the size and degree of interlocking of the crystals is increased. The *rate of firing* in the kiln may also affect the strength; if too rapid it may cause cracks or 'bloating' in the articles.

The *duration of the firing* also affects the strength of the articles when cold, because prolonged heating at a sufficient temperature produces an increase in the proportion of fusible bonding material. Hence it is not only necessary for the final temperature attained in the burning to be sufficiently high, but in many cases it is equally necessary to maintain the kiln at that temperature for a sufficient time to enable the maximum strength of the contents to be developed. This is especially the case with porcelain (also with silica and magnesia bricks) in which special reactions must occur before the maximum strength is obtained, but it is also important with many other ceramic materials.

The *atmosphere* in which the goods are fired may influence the strength; some, such as red bricks, firebricks, and most refractory materials are fired, as far as possible, in an oxidising atmosphere, as this ensures a material which will have the greatest strength at high temperatures, but if some of the same materials (which contain ferric oxide or its equivalent) were fired in a reducing atmosphere, their strength, when cold, would be greatly increased, because of the larger proportion of bond formed. A reducing atmosphere greatly reduces the resistance of refractory materials, and of most ceramic materials containing ferric oxide, to load at high temperatures.

The *cooling of the kiln* or oven also affects the strength of the contents, as too rapid a cooling may produce fine cracks or 'dunts' in the ware. Articles made of silica, magnesia, and vitrified ware are particularly sensitive in this respect, and articles made of them, therefore, should be very carefully cooled after firing. The cracks produced are frequently so small as to escape notice when the articles are immediately withdrawn from the kiln, but they greatly reduce the strength of the ware.

With some materials, such as most clay products, the actual rate of cooling need not be detrimental if it is effected by passing a large volume of air, at a temperature

¹ Wiechula, B. A. and Roberts, A. L., *Trans. Brit. Ceram. Soc.*, 51, 173, 1952.

only slightly below that of the contents, through the kiln. The cracks and other defects attributed to rapid cooling are chiefly due to the great difference between the temperature of the articles and that of the air admitted to the kiln. In other materials, however, the rate of cooling is important, especially where a critical range of cooling has to be passed through, as in the case of silica; the rate of cooling must then be regulated so as to effect all the necessary physical or chemical changes desired and yet prevent any undesirable ones. Such regulation can only be learned by constant inquiry. An investigation of the critical range of cooling of various porcelains and other ceramic materials would probably result in a decrease of the total time required for cooling the kilns and would also reduce the proportion of cracked and dunted ware.

Repeated changes of temperature, especially in the case of refractory materials, gradually reduces their strength to an extent depending on (a) the coefficient of expansion or contraction of the material, and (b) the chemical and physical changes which may take place during the repeated heating and cooling. Materials such as silica and magnesia, which are very sensitive to sudden changes in temperature, soon lose so much of their strength as to become useless unless carefully treated (see also Chapter XII).

Repeated Heating. When fireclay and grog bricks are repeatedly heated to a high temperature, their resistance to blows is reduced; this reduction is attributed by Mellor and Austin to:

(a) The volatilisation of alkalis and silica, which results in a reduction of the mechanical strength.

(b) The irregular contraction of the mass as a result of the presence of irregular patches of crystals formed by chemical reactions, which occur on repeatedly heating the material.

(c) Crystallisation or glass formation which occurs when clays are repeatedly heated at temperatures above 800° C. for long periods of time.

Fireclay bricks and other siliceous refractories may undergo pronounced changes when heated repeatedly and maintained at high temperatures for prolonged periods. Crystallisation of mullite may take place and the crystallite size may increase considerably. Furthermore, some alumino-silicates lose strength and rigidity at high temperatures owing to the development of an ever-increasing quantity of glass. The precise reasons for this is not known with certainty, but it has been suggested that it is due to quartz gradually dissolving in the liquid phase. A more likely explanation is that prolonged heating results in more uniform distribution of the available fluxing elements and the formation of more liquid phase.

The effect of repeated heating and cooling on quartz glass or fused silica is very slight provided the temperature does not exceed about 1100° C. Heating to higher temperatures causes a severe loss of strength, along with a change in other properties, due to the crystallisation of cristobalite.

The **temperature during use** has an important influence on the strength of ceramic materials, because their strength is usually much lower at high temperatures. They retain their original (cold) strength until a temperature is reached at which the bonding material begins to soften and yield under pressure, or at which, as previously

mentioned (p. 670), the fluxes present in the material begin to soften or fuse and so decrease the strength of the mass at the high temperature to which it is exposed. In this way, fluxes play a double part, as they reduce the strength of a ceramic material at high temperatures and increase it at lower ones.

The strength of refractory materials when hot is often more important than the strength when cold, as the latter is usually ample, whilst the former is not merely lower, but is often an unknown factor. Moreover, as the strength when cold is usually much greater than the strength when heated, any material which is sufficiently strong at the highest temperature attained during its use, is almost certain to be perfectly satisfactory at ordinary temperatures.

As most ceramic materials are not quite pure, they do not usually possess a sharply-defined softening or yielding point when heated, and consequently their crushing strength diminishes gradually over a long range of temperature; this is still more noticeable if the material be subjected to a considerable pressure or load which is not intense enough to crush the cold material, but causes it to lose its shape rapidly when any softening of the bond or other fusible constituent occurs. If the material under examination consists of a single pure substance, such as pure silica, however, the strength remains fairly constant until the fusion-point is reached and loss of shape then occurs suddenly, especially if the material is under pressure.

That the long range of temperature through which some materials lose strength progressively is due solely to the gradual production of fused or partially fused material is clearly shown by varying the pressure or tensional stress applied to the material, when it will be found that loss of shape occurs at a lower temperature when the pressure or tension is greater and *vice versa*. When only a very small amount of mobile materials has been formed a much greater stress is required to deform the mass and to cause the unfused particles to move through or in the fused portion. As the temperature increases, or the time of heating is prolonged, more and more fused and mobile material is formed and less stress is needed to move the remaining particles.

The fact that most ceramic materials have a much lower strength at high temperatures than when in the cold state, is very important in connection with their use in the construction of furnaces, retorts, crucibles, and other refractory articles.

When an essentially crystalline material is being used, a high strength is generally maintained up to a comparatively high temperature; on the other hand, glassy-bonded refractories begin to soften at low temperatures and progressively lose strength on further heating. An important property of refractories is their *refractoriness-under-load*, i.e. their ability to withstand high temperatures without undergoing deformation under an applied force.

The refractoriness-under-load of a refractory material is usually carried out on a cylindrical specimen of 2 in. diameter and $2\frac{1}{2}$ in. long cut from a brick or other shape.¹ This is placed on alumina or silicon carbide blocks B, in a carbon granule resistance furnace F, and a load L applied to it by weights through a system of levers to an alumina thrust rod R (Fig. XIII.3). The specimen is heated at a fixed rate (10° C. per min. is recommended for fireclays) and the change in length measured on a suitable recording instrument. This rate of *rising temperature* may be maintained

¹ Blocks $2\frac{1}{2}$ in. \times $1\frac{1}{2}$ in. \times $1\frac{1}{2}$ in. are preferred by some workers.

until the test piece fails, i.e. shears or suffers a contraction of 10 per cent or more, or a certain *temperature may be maintained* and the time required for the specimen to fail is recorded. In the former test it is usual to record the initial softening point, the point of rapid failure (corresponding to a shrinkage of 1 per cent per min.) and the temperature of complete failure.

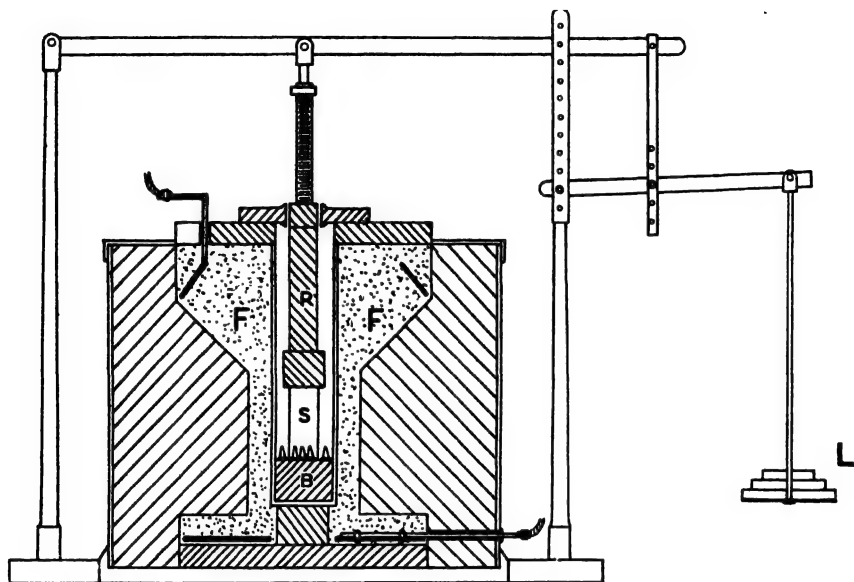


FIG. XIII.3. AN APPARATUS FOR MEASURING THE REFRACTORINESS-UNDER-LOAD

There are no standard conditions generally adopted in Great Britain under which the refractoriness-under-load is measured;¹ the conditions are suited to the sample being tested. A most important consideration is to ensure that the specimen is heated uniformly and evenly throughout and that oxidising conditions prevail at all temperatures. Carbon granule resistance furnaces are much more serviceable than gas-fired ones especially at the high temperatures which are encountered in testing high-grade fireclays and siliceous products; the measuring thermocouple should be in contact with the specimen.²

Lahr and Hardy³ have described an ingenious modification to the apparatus in which an inner lining to the furnace is not only rotated (a refinement introduced by Cross⁴) but oscillated in a vertical direction relative to the specimen. They claim that the refractoriness-under-load of silica specimens thus measured is very reproducible and can be correlated with the amount of alumina present as impurity, provided that a slow rate of temperature rise (1° C. per min.) is employed.

¹ See B.S.S. 1902, 1952.

² Some workers prefer to use Seger cones to measure the temperature or duration of heating. These should be positioned near to the specimen (see Fig. XIII.3).

³ Lahr, H. R. and Hardy, C. W., *Trans. Brit. Ceram. Soc.*, 56, 369, 1957

⁴ Cross, A. B., *Trans. Brit. Ceram. Soc.*, 54, 461, 1955.

The test is normally carried out under a load of 28 lb. per sq. in. (2 kg. per sq. cm.) or 50 lb. per sq. in.

The American Society for Testing Materials specifies that the refractoriness-under-load should be measured on a full brick under an applied force of 25 lb. per sq. in.; a slow heating rate is also recommended.

The refractoriness-under-load properties of some refractory materials under a load of 50 lb. per sq. in. are shown in Fig. XIII.4 and Table XIII.X.

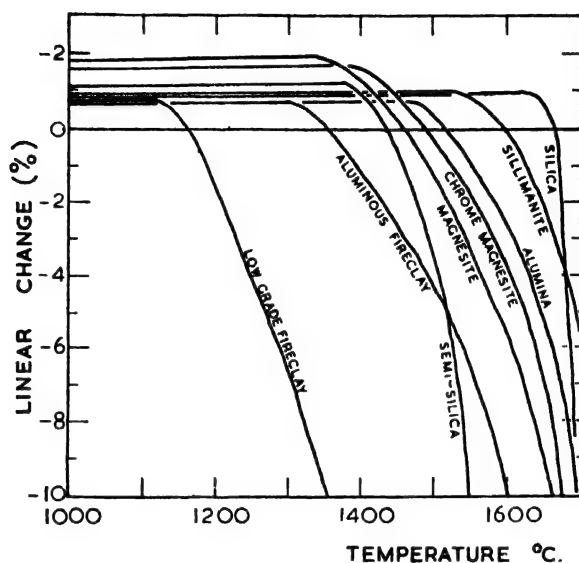


FIG. XIII.4. THE REFRACTORINESS-UNDER-LOAD OF VARIOUS REFRACTORY MATERIALS

TABLE XIII—X REFRACTORINESS-UNDER-LOAD CHARACTERISTICS OF SOME REFRACTORY BRICKS

	Fireclay (low grade)	Fireclay (42 per cent Al_2O_3)	Silica	Dolomite (semi-stable)	Magnesite	Chrome- magnesite
Initial softening	1135° C.	1320° C.	1670° C.	1350° C.	1400° C.	1420° C.
Rapid softening	1260	1450	1690	1520	1540	1555
Final failure	1350	1590	1710	1600	1620	1680

The effect of different applied pressures on the failure of some materials is shown in Fig. XIII.5. Glassy-bonded materials, such as fireclays show pronounced changes in the refractoriness-under-load properties with different applied loads, but silica bricks show little change.

The refractoriness-under-load properties of aluminosilicate refractories depend on their chemical and mineralogical composition. Such refractories yield

when a sufficient quantity of liquid has formed which flows when the body is subjected to pressure. Not only is the amount of liquid important, but also its physical nature (which depends largely on its chemical composition) and also the rheological behaviour of the crystal and liquid system.

In general, refractory materials with a high alumina content have a high yield point under load, but the type and amount of fluxes (compounds of iron, calcium, magnesium, sodium and potassium) which may be present are important factors.

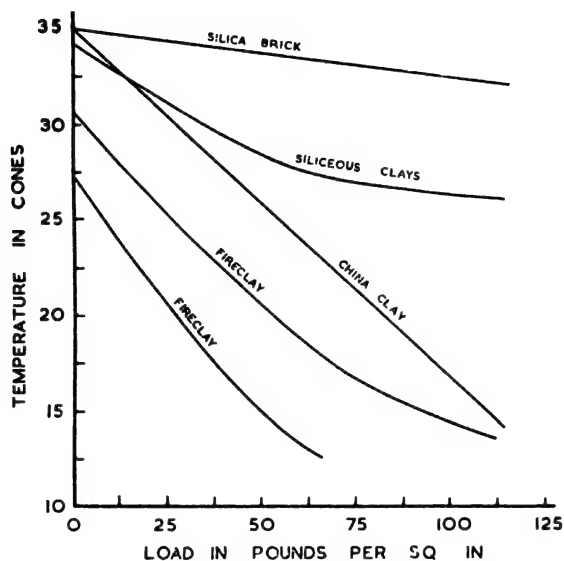


FIG. XIII.5. THE REFRACTORINESS OF SOME MATERIALS UNDER VARIOUS APPLIED PRESSURES

Well-developed crystals or hard-fired grog can increase considerably the yield point of an aluminosilicate refractory; hence an article prepared from kyanite or sillimanite containing large crystals of mullite is often superior to bodies containing a higher proportion of alumina but prepared from bauxitic clays.

Quartz behaves in a similar way so that the load-bearing properties of some siliceous fireclays at high temperatures is remarkable. Coarsely-grained quartz is unreactive in aluminosilicate bodies up to about 1350° C. and it has valuable stabilising properties to these temperatures. At high temperatures, however, quartz is rapidly attacked and although it may increase the initial yield point, the rate of subsidence above this point is extremely rapid. This effect is illustrated by the figures in Table XIII.XI which were obtained on aluminosilicate refractories when tested under a load of 28 lb. per sq. in.

Aluminosilicate refractories with a high proportion of crystalline material are less prone to differences in behaviour when tested under different applied pressures than are those with a high proportion of glassy bond. The initial yield point of silica,

sillimanite and alumina refractories are little different when tested under a load of 28 or 50 lb./sq. in., but with fireclays, particularly the non-siliceous variety, differences in yield point of up to 100° C. may be recorded between the different pressures.

It is common practice to test all aluminosilicate refractories under a load of 28 lb./sq. in., but 50 lb./sq. in. is more favoured for silica.

TABLE XIII—XI. REFRACTORINESS-UNDER-LOAD PROPERTIES OF SOME ALUMINO-SILICATE ARTICLES

Type of Refractory:	<i>Silica brick</i>	<i>Semi- silica</i>	<i>Sili- ceous fireclay</i>	<i>Low alkali fireclay</i>	<i>High alkali fireclay</i>	<i>Silli- manite</i>	<i>Alu- minous</i>	<i>Alu- mina</i>
Percentage of Alumina:	0.3	15	27	42	40	63	72	90
Initial softening	1690	1445	1400	1400	1350	1530	1490	1550
Rapid softening (5% subsidence)	1700	1490	1480	1500	1440	1610	1580	1620
Final failure (10% subsidence)	1720	1520	1510	1610	1525	1745	1695	1730

The loss of strength at high temperatures may be due to:

(a) Chemical rearrangement of the constituents of the mass with the production of liquid.

(b) Physical breakdown due to melting of crystal components.

(c) Structural defects which develop during the heating.

Effect of Weathering on Strength. Exposure to weather greatly decreases the strength of most ceramic articles, those composed of clay which has merely been dried being the most affected. Most building bricks and roofing tiles are very resistant to weathering, but this is not the case with firebricks which may lose from 1–21 per cent of their crushing strength after six months, and 11–28 per cent after twelve months' exposure. One brand of specially strong machine-made bricks was found to withstand six months' exposure to the weather practically without loss in strength. Some very porous hand-made fireclay bricks are greatly reduced in strength on exposure and may be made practically worthless after six months' exposure.

Silica bricks may lose as much as 39 per cent of their crushing strength when cold if they are exposed to the weather for twelve months, whilst some magnesite bricks decrease in crushing strength by 15 per cent after six months' exposure and 33 per cent after twelve months' exposure. The strength of magnesite bricks when heated under load is also affected; some bricks, after being weathered for twelve months, failing at a temperature of 40° C. lower than new bricks under a pressure of 25 lb. per sq. in. Some magnesite bricks are more seriously affected by the weather than almost any other kind of refractory brick and much greater care is therefore required in their storage.

The reduction in strength of ceramic articles on exposure to weathering conditions is intimately related to their permeability or the ease with which water can penetrate. The slightly solvating action of rain water is sufficient to cause a loosening of the bonds within the mass thereby resulting in an overall loss of strength.

Effect of Frost on Crushing Strength. The crushing strength of articles is reduced by subjecting them to the action of frost, as shown in Table XIII.XII, due to J. C. Jones.¹

The effect of freezing does not appear to be related to the original strength of the brick, but to depend upon other factors such as texture, porosity, temperature and duration of burning, etc. Some curiously contradictory results are sometimes obtained when the crushing strengths of bricks, etc., which have been repeatedly subjected to freezing, e.g. in a refrigerator, are determined.

TABLE XIII—XII. EFFECT OF FREEZING ON CRUSHING STRENGTH

Kind of Brick	Hardness	Crushing Strength lb./sq. in.		Per cent Loss in Strength	Per cent Pore Space
		As received	Frozen		
Plastic surface clay	Soft	1374	1194	13.1	33.0
	Med. soft	3400	3567	4.6*	26.9
	Med. hard	5315	4289	19.9	21.2
	Hard	7260	7377	1.6*	10.2
Plastic shale	Soft	2913	2671	8.6	26.2
	Med. soft	5793	4625	20.2	17.8
	Med. hard	10143	8522	16.5	11.6
	Hard	11470	7606	33.8	5.8
Wire-cut shale	Soft	4637	3729	19.6	27.6
	Med. soft	8117	6965	14.2	17.1
	Med. hard	11315	9165	19.4	2.1
	Hard	11997	11500	4.1	0.9

* Increase.

The effect of various factors, such as porosity and hardness, on the frost resistance of fired materials has not been investigated fully. The amount and extent of water penetration is obviously important, but the size of the pores is a critical factor. The elasticity of the material itself must also be considered, because a brittle mass is more liable to be fractured by the force exerted by the expansion of melting ice.

The soluble salt content of bricks has a pronounced influence on the resistance to weathering and frost erosion; the greater the amount, the more readily is water absorbed into the material, therefore a high content of soluble salts should be avoided. They may also exert a chemical action which rapidly reduces the strength of the bricks, for when sulphates are the source, the water absorbed is rendered slightly acid.

W. N. Thomas² has investigated the mechanism of frost action on building bricks and has deduced empirical relationships which link the probable influence of

¹ *Trans. Amer. Ceram. Soc.*, 9, 567, 1907.

² Thomas, W. N., *Building Res. Stn. Tech. Paper*, No. 17 (H.M.S.O., London, 1938).

the total water absorption, the saturation coefficient, and the compressive strength on the resistance to frost. The saturation coefficient is defined as the ratio between the amount of water absorbed (C) after 24 hours' immersion in cold water to that absorbed (B) after boiling the brick for 5 hours in water and allowing it to cool whilst still immersed.

Bonnell and Butterworth¹ have suggested that if the total water absorption (B) is not greater than 7.0 per cent by weight, or if the saturation coefficient (C/B) is less than 0.60 or if the compressive strength of the fired brick is greater than 7,000 lb./sq. in. then even severe exposure conditions will not appreciably reduce the durability of the brick. Even when none of these conditions are fulfilled the brick will still be resistant provided that $B + 100C/B$ is not greater than 72. Should this relation be between 72 and 93, the durability of the bricks is doubtful. Bricks with a figure of greater than 93 would be most liable to break up under severe conditions although under normal conditions they might be quite satisfactory if they had been well fired and had only a low content of soluble salts.

Effect of External Chemical Agents on the Strength

(a) *Deposited carbon.* Some fireclay bricks are exceptionally prone to lose strength when exposed to furnace gases, rich in carbon monoxide. The cause of failure is attributed to the deposition of carbon in the region of iron spots within the structure of the fired material.

The carbon fills pores and voids in the vicinity of the iron spots and forces the bricks apart, and characteristic flaking may then occur. The reduction in strength takes place only in alumino-silicates rich in iron spots. In well-fired materials little trouble is encountered because the iron is mostly converted to a silicate which does not catalyse the formation of carbon.

(b) *Slags and Flue-dust.* When in contact with molten slags at high temperatures, most ceramic materials are subjected to considerable erosion. In addition, the slag may penetrate the pores of the material and cause a considerable reduction in strength, especially at high temperatures. The slag may force apart the grains of the brick or it may chemically combine with the material of the brick and form low-melting compounds or liquid. Dusts which are carried in furnace gases may behave in a similar fashion.

STRENGTH OF CLAYS AND CLAY PRODUCTS

THE strength of various ceramic materials depends on the factors mentioned on pp. 759-81. In some cases, the strength is a very important characteristic, but in others it is not so important and may be sacrificed to secure other properties.

Strength of Raw Clay and Clay Pastes. The strength of raw clays and clay pastes, i.e. of clays in the plastic state, varies very greatly. Some lean clays will break under a tension of a few ounces, whilst other highly plastic clays such as bentonites may withstand a tension of several pounds per square inch. The duration of the application of the force also affects the result, as a small force acting throughout a

¹ Bonnell, D. G. R. and Butterworth, B., 'Clay Building Bricks of the United Kingdom', *Nat. Brick. Advis. Council*, Paper 5 (H.M.S.O., London, 1950).

long period will have an effect similar to that of a much larger force acting for a much shorter time.

The *green strength* (i.e. the wet strength) of a clay or other ceramic material is an important consideration, especially when the moulded shape has to be handled or transported prior to drying. As the strength varies with the plasticity of the clay and with the proportion of clay and water present, no definite figures can be usefully published. Plastic clays are usually much stronger in the raw state than shales and indurated clays.

Strength of Dry Clays. The strength of ceramic materials in the dried condition is often important, for, obviously, the dried articles must be sufficiently strong to withstand the amount of handling to which they are likely to be subjected and also the weight of any articles placed above them when they are set in the kiln. Such articles as tiles must be particularly strong when in the dry state. Some pieces of pottery also require to be made of material of considerable strength when dry.

The fundamental causes of the strength of dry clays are not known with certainty. Undoubtedly the more points of contact there are within the mass and the smaller the void space the greater will be the strength, but the proportion of fine particles or colloidal material is of great importance. Theories have been propounded which link dry strength with (a) attractive forces between the particles; (b) a continuous water film surrounding the particles which is not removed, except by heating at high temperatures; and (c) the union of the ionic fields of surface layers; none of these theories can be established with certainty.

Like clays in the plastic state, dried clays vary greatly in tensile strength; in some, it is as low as a few pounds per square inch, whilst in others it may be as high as 400 lb. per square inch. Brick clays in the dry state have usually a tensile strength of about 100 lb. per square inch. Clays which have the greatest plasticity when in the form of a paste usually have the greatest strength when dry.

Some clays are of value principally for the strength they impart to other materials with which they are mixed before the body is moulded and dried. Examples of this type are the bond clays, which are used to impart strength to sand mouldings for metal casting purposes, and ball clays, which are used to strengthen whiteware bodies and at the same time produce a white, fired product. The strength of brick clays and fireclays is variable, but, in general, it is less than that of the bond or ball clays, but greater than that of the residual kaolins.

The main factor influencing the dry strength of clays is undoubtedly the fineness of particle-size or the available surface area per unit weight of material. Thus, montmorillonite-type clays, such as the bentonites, where the particle-size is extremely small, are far more adhesive than any other type of clay. Similarly, clays containing the mineral, *livesite*, which is inherently fine-grained, are capable of imparting greater strength than true kaolinites. Table XIII.XIII shows the tensile strength of test pieces made of silver sand, bonded, in each case, with 5 per cent of clay of different type.

The dry strength required will depend on the nature of the articles to be made; exceptionally thin products, such as tiles or pottery require to be strong when dry in order to avoid damaging in handling. As the cohesive power of most materials in

the raw and dried states is low compared with that in the burned condition, they must be carefully handled so as to avoid damage.

Strength of Burned Clay Wares. The strength of articles, etc., made of burned clay varies according to the materials used and the mode of manufacture, very great variations sometimes occurring in articles made under apparently identical conditions. The need for careful control is, therefore, very evident.

TABLE XIII—XIII. TENSILE STRENGTH OF SAND BONDED WITH
5 PER CENT OF CLAY OF DIFFERENT TYPES

Type of Clay	Tensile Strength	Type of Clay	Tensile Strength
	lb. per sq. in.		lb. per sq. in.
Montmorillonite clay	823	Fireclay (Shropshire)	170
Bonding clay (Irish)	220	" (Yorkshire)	50-92
(Scottish)	225	Brick clays	40-120
Ball clay (Devon)	175	Brick shales	35-91
(Dorset)	187	Sedimentary kaolins	50-105
		Residual kaolin (Cornwall)	30

The strength of *building bricks* varies through wide limits and depends entirely on the amount of glass which has developed under the conditions of firing, and on the final porosity. Bonnell and Butterworth¹ adopt an arbitrary scale of values for such bricks as follows:

Description	Compressive Strength (lb. per sq. in.)*
Very low	Less than 1,000
Low	1,000-2,000
Fairly low	2,000-3,000
Medium	3,000-5,000
Fairly high	5,000-7,000
High	7,000-10,000
Very high	Greater than 10,000

* To convert lb. per sq. in. to tons per sq. ft. divide by 15.6.

Most building bricks have a compressive strength in excess of 2,000 lb. per sq. in., otherwise, there may be too great a loss caused by chipping and fracture during transportation. An average figure would be in slight excess of 3,000 lb. per sq. in. although there are many bricks with strengths up to 7,000 lb. per sq. in. **Facing bricks** do not require to be as strong but in practice many are equally strong because a greater firing temperature may be employed to ensure a good colour.

The American Society for Testing Materials classifies facing and building bricks into three groups depending on the degree of frost and weathering they will

¹ Bonnell, D. G. R. and Butterworth, B., see p. 781.

have to withstand (Code C216-50). They each must conform to certain minimum strength requirements when tested by standard methods. The grades and specifications are as follows:

Grade	Exposure conditions	Minimum compressive strength (flatwise) (lb. per sq. in.)	
		Average of 5	Individual
SW	Severe frost and weather	3,000	2,500
MW	Medium weathering	2,500	2,200
NW	Inside wall, no exposure	1,500	1,200

Engineering bricks or vitrified bricks must have a compressive strength of at least 7,000 lb. per sq. in. and some are manufactured with values in excess of 20,000 lb. per sq. in. (see British Standard 1301:1946).

Paving bricks are not used so frequently nowadays in this country, although they are still valued in some other countries for their characteristic hard wearing properties. These bricks are required to be strong and hard and to combine all the qualities expressed by 'toughness'. They must also be very uniform in strength, as if a soft brick is used with a number of harder ones it will be worn away more quickly and will cause a depression which will soon result in chipping of the adjacent bricks by passing traffic. For this reason, the variation in the strength of such individual bricks should not differ much from the average strength of all the bricks used on a job. As paving bricks are subjected to repeated blows rather than to great pressure, their effective strength is best estimated from the results of the 'Rattler Test' described on p. 800.

According to G. H. Brown,¹ in order that paving bricks may give good results when in use, they should not lose more than 22 per cent of their weight when subjected to the standard 'rattler test'. Some bricks which he examined showed 23-27 per cent, and gave good service, but those showing a loss of more than 27 per cent were invariably of low durability. The National Brick Manufacturers' Association specifies that paving bricks tested by the standard 'rattler test' should never lose more than 18 per cent of their weight and the average loss on one charge of bricks should not exceed 14 per cent of the original dry weight.

The modulus of rupture of good paving bricks when tested by the standard cross-breaking test is 1500-3500 lb. per square inch, the average being 2000-3000 lb. per square inch. It will usually be found that the cross-breaking strength in individual bricks varies from 8-30 per cent on either side of the average of a large number of bricks and the usual variation is about 20 per cent. This variation is due to irregularities in the material and in the process of manufacture. The American National Brick Manufacturers' Association specifies for paving bricks a modulus of rupture of not less than 2500 lb. per square inch and the average strength of three bricks should not be less than 2700 lb. per square inch when tested by the standard method.

¹ *Trans. Amer. Ceram. Soc.*, 16, 364, 1914.

The strength of porous clay wares, such as **porous pipes, tiles, terra-cotta**, etc., is generally about the same as that of building bricks. Articles containing a larger proportion of vitrified material are stronger, and highly vitrified ware, such as stoneware, has a strength approximating to that of blue or vitrified bricks.

Earthenware and **china** vary considerably in strength, the former being usually much weaker than the latter and the latter being usually rather weaker than other forms of porcelain.

Porcelain invariably has a high strength because of the glassy nature of the fired material, although different samples vary because of the raw materials used and the mode of manufacture. Compressive strengths of about 40,000 lb. per sq. in. are quite common in ordinary felspathic porcelains, whilst the best high-tension electrical porcelains may withstand a load of 65,000 lb. per sq. in. The tensile strength which for some purposes is more important varies from 1,500 to 13,000 lb. per sq. in.

Electrical porcelains made of steatite have compression strengths of 60,000–150,000 lb. per sq. in.; those of zirconia 75,000–95,000 lb. per sq. in.; rutile and titanate bodies 50,000–130,000 lb. per sq. in. Cordierite and porcelain bodies have much lower tensile strengths¹ (of the order 2–6 lb. per sq. in.) than zircon porcelain (13 lb. per sq. in.), steatite (8–12 lb. per sq. in.), and titanates (6–10 lb. per sq. in.). Glazed porcelains are usually stronger than unglazed ones.

The crushing strength of **fireclay bricks** varies according to the temperature at which they have been burned and depends on the extent to which the particles are bonded together with fused matter. As a general rule, the higher the temperature at which such bricks are burned, the greater will be their strength when cold. Fire-bricks should be at least strong enough to withstand mechanical handling and to resist the weight of any superimposed structure.

The Standard Specification for Refractory Materials for the Gas and Coking Industries requires cold crushing strengths of at least 1,800 lb. per sq. in. for E and F grade bricks and 2,000 lb. per sq. in. for G and H grades (see p. 730).

The transverse strength of fireclays usually lies between 500 and 700 lb. per sq. in.

In general, the compressive strength of alumino-silicate refractories increases with increasing alumina content; this is, however, related more to the greater precision with which high-grade bricks are made, than to any chemical or physical reason.

It is customary to add 'grog' or pre-calcined clay to the fireclay batch in order to reduce the firing shrinkage. If this material is added in too great a quantity, the strength will be drastically reduced and the bricks will be of little value. Care should be taken when deciding the amount of grog to be used, that the clay content is sufficient to produce a strong body at the temperature of firing.

The crushing strength of fireclays and other alumino-silicates at high temperatures is usually of greater importance and is dependent on the nature and amount of the glassy phase and/or the crystalline development.

Fireclay bricks and other alumino-silicate refractories should be selected so that there is little or no deformation or loss of strength at the temperatures of use, as when they are built into a setting and have to withstand the weight of the overlying structure.

¹ Tensile strengths quoted should be multiplied by a factor of 10³.

Hollow refractory ware should be very strong, so as to resist the pressure of the contents at high temperatures. Thus, **crucibles** should have both a high tensile and a high crushing strength, as they are liable to be 'pulled' by the weight of their contents and to be crushed by the pressure of the tongs. In order to secure the maximum tensile strength when hot, the clays used in the manufacture of crucibles should have a high-bonding power and the particles of aggregate should interlock well. The porosity of such refractories should be as low as possible to avoid penetration by the liquid metal.

Glasshouse pots (used for making and transporting molten glass) must be very strong in order to withstand the pressure of the charge at high temperatures. They must also have a low porosity to reduce the degree of glass penetration.

Retorts require to be very strong to resist (a) the weight of the setting and the superimposed structure; (b) the weight of the contents of the retort or the pressure they exert upon it; and (c) the rough handling to which they are subjected, such as when the retorts are being filled or emptied.

Saggars are required to be very strong at the maximum temperature attained during the firing of the particular goods for which they are used, in order that, when filled, they may be piled one above another without the pressure of the upper saggars causing the collapse of the lower ones. Pieces cut from saggars give no indication of the crushing strength of saggars as a whole, and determinations of the crushing strength of whole saggars appear to be misleading owing to the difficulty of applying the pressure uniformly.

STRENGTH OF OTHER REFRACTORY MATERIALS

Silica and siliceous raw materials are, in common with most other forms of non-clay bodies, relatively non-plastic; consequently, a moulded shape can only be strong in the wet or dry state provided that some plastic or adhesive material has been added. When fired, such refractories do not readily develop a liquid and the cementing of the structure to form a strong body is usually the result of solid reactions which take place initially at the points of contact of individual particles. The strength, therefore, largely depends on the grading of the raw material (see p. 373) and the duration and temperature of the firing.

Silica bricks owe their strength to the felted mass of crystals of cristobalite and tridymite which are formed on heating quartzitic materials in the presence of a mineraliser such as lime. Some glass is invariably present, but whether it simply fills the pores between the crystallites, or is influenced by the silica minerals with which it is in contact is not known, but it does not behave like the glassy phase of clays or like fused silica, which melt and begin to flow at comparatively low temperatures. Silica bricks are strong at normal temperatures and maintain that strength almost up to their melting point of about 1700° C. Failure of such materials at high temperatures is not gradual, as is the case with bodies rich in glass, but takes place suddenly with only a short interval between the point of initial deformation and that of final collapse (see Table XIII.X. and Fig. XIII.4). (See p. 777.)

The presence of impurities in siliceous materials has a pronounced influence

on the temperature of failure; alumina is particularly serious for a reduction of about 10°C . occurs for each 0.1 per cent of this oxide which is present.

Because silica bricks maintain their strength even at high temperatures they are greatly valued for use in furnace settings where the refractory is subjected to large stresses at elevated temperatures. High grade material is capable of withstanding temperatures up to 1670°C . without appreciable deformation and consequently is a valuable refractory, particularly in settings which are subjected to considerable stress. The roofs of many basic open hearth furnaces are constructed of silica, which is stronger at high temperatures than any basic refractory. Although the acidic material is more readily attacked by slags and flue dusts, this may be minimised by keeping the porosity as low as possible.

Well-fired silica bricks may have cold crushing strengths in excess of 6,000 lb. per sq. in. This is important when large unsuspended structures have to be built; basic materials are, in general, heavier and not so strong and collapse more readily.

The Gas and Coking Industries specify that silica bricks should have a minimum crushing strength of 2,500 lb. per sq. in.

Silica bricks do not have a high transverse strength and most of them fail under 600 lb. per sq. in.

Semi-silica bricks are usually not very strong because of their heterogeneous nature and the high proportion of non-plastic quartz which they contain. It is advisable, however, that their compressive strengths should exceed 1,500 lb. per sq. in.

Bauxite, Diaspore, Aluminous, Sillimanite and Mullite bricks should have cold crushing strengths of at least 1,000 lb. per sq. in. Such bricks however, are difficult to hard-fire because of the high temperatures involved, so that they are not generally so high in strength as other refractory products. *Fused mullite* bricks are extremely strong.

Thermal Insulating Bricks are usually weak because of their extremely porous nature. Diatomite and vermiculite shapes have crushing strengths of only 135–500 lb. per sq. in. Insulating bricks made of fireclay, silica, bauxite or kyanite and those made of basic materials are stronger—viz. 500–1,300 lb. per sq. in., but their strength falls rapidly at high temperatures.

Basic bricks should be as strong as possible to withstand the weight of molten metal and slag with which they are in contact, and to withstand the weight of overlying brickwork. The cold crushing strength of basic bricks is usually in the range 2,000–4,000 lb. per sq. in. Dolomite bricks are, on average, the strongest, and chrome-magnesites are better than magnesites. The transverse strengths of basic bricks are greater than those of fireclay and silica, being of the order of 1,300 lb. per sq. in.

Basic refractories, such as magnesite, dolomite, chrome-magnesite and other composite materials are non-plastic and only develop strength as a result of crystalline formation when fired. Their strength depends largely on the type of crystals and the amount of intergrowth and these factors also determine the behaviour at elevated temperatures. Thus, in magnesite bricks, some low melting crystals, such as merwinite $3\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$ or calcium ferrite $\text{CaO} \cdot \text{Fe}_2\text{O}_3$ are usually present

which cause failure at low temperature; in chrome-magnesites on the other hand, the composition is so adjusted as to reduce the content of these deleterious compounds and as a consequence the strength is maintained to higher temperatures (see Table XIII.X. p. 777). Chrome-magnesite refractories have a lower tensile strength at high temperatures than have magnesites, a factor which limits their use as roofing materials in open-hearth furnaces.

STRENGTH OF GLASS AND SIMILAR MATERIALS

Glass, being a uniform, non-porous body with a continuous structure, is stronger than a non-vitrified mass of packed particles; though it is a relatively weak material compared to metals, is usually *brittle* and is extremely variable in strength. Turner and Holland,¹ for example, found that the modulus of rupture of several identical specimens cut from the same sample of sheet glass varied from 750 Kg/cm² to 1600 Kg/cm² and differences of a similar order have been reported by other investigators.

The mechanical strength of glass depends on many factors, some of which are:

- (a) The composition and crystalline linkages of the material.
- (b) The degree of perfection in the glass. Microcracks are a frequent source of low strength.
- (c) The 'flow-orientation' in the sample. Glasses which have been extrusion cast or drawn may have different strengths when tested along several directions due to the differences in crystal development.
- (d) The method of applying the breaking force. Glass is a super-cooled liquid and deforms progressively under an applied load.
- (e) The temperature at which the test is carried out. As the temperature is raised the viscosity of glass falls and a gradual reduction in strength takes place.

Glass is to some extent elastic, that is, it can be deformed by an applied force but it readily regains its original shape when the force is removed. It is this property which is of importance in *glazes*, which frequently are subjected to strains arising from the expansion or contraction of the body. Like all brittle solids, glasses have a much greater compression than tensile strength. The usual range is: Compression strength 110×10^3 to 130×10^3 lb. per sq. in. and tensile strength 7×10^3 — 13×10^3 lb. per sq. in.

The tensile strength of glasses depends greatly on the diameter of the test-piece, glass-fibres have tensile strengths from 15×10^3 to 900×10^3 lb. per sq. in. By *tempering* (i.e. heating well above the annealing temperature and then blowing cold air uniformly over both surfaces) the surface layers are in strong compression and the interior is in tension so that the total strength is greatly increased. Thus, a glass which has been well annealed and has a transverse breaking strength of 7,000 lb. per sq. in. will probably have a transverse breaking strength of 25,000–30,000 lb. per sq. in. after being tempered.

The brittleness of glass is greatly reduced by *lamination*, i.e. causing two sheets to adhere by the insertion of polyvinyl butyral or other suitable, light-stable resin

¹ Holland, A. J. and Turner, W. E. S., *J. Soc. Glass. Tech.*, 20, 72, 1936.

which, on the breaking of the glass by sudden impact, leads to small radiating cracks and avoids the 'flying' of the glass.

Quartz-glass or vitreous silica has a crushing strength of 200,000–300,000 lb. per sq. in. and a tensile strength of 11,000–13,500 lb. per sq. in., these it retains up to about 1400° C. but softens rapidly at higher temperatures.

THE STRENGTH OF GLAZES

THE strength of glazes has not been investigated to any great extent, yet it and the elastic modulus are important in connection with the avoidance of cracks and 'peeling'.

The elastic modulus of stoneware glazes is generally between 5700 and 6800 kg. per sq. cm., that of lead glazes is lower than for leadless ones though the variation in the figures obtained by different observers makes it uncertain whether any real relationship exists between them.

The tensile strength of glazes is of more importance than the crushing strength. The tensile strength of stoneware glazes is about 5 to 8 kg. per sq. mm., though some glazes have much lower strengths.

DETERMINATION OF STRENGTH OF CERAMIC MATERIALS

THE principal methods of determining the strength of clays and other ceramic materials, are naturally based on the various forms in which the 'strength' of these materials is exhibited. According to the information required, a method is used which determines one or more of the following: (1) tensile strength; (2) compression or crushing strength; (3) transverse strength or modulus of rupture; (4) resistance to impact; (5) torsional strength; (6) modulus of elasticity; (7) deformability; (8) the 'rattler' test; (9) resistance to repeated freezing.

Some of these methods may be applied either to the cold material or to it at any suitable temperature. The strength of a material or article at the temperature at which it is used is, in many cases, of much greater importance than its strength at atmospheric temperatures. This is especially the case with refractory materials.

Tensile Strength. The tensile strength of ceramic materials is most conveniently determined in the same manner as that of Portland cement, though when very weak materials, such as plastic or dry clay, are being tested a lighter and more sensitive machine is preferable. The test piece usually employed for making tensile tests consists of an 8-shaped block of material, the ends being $1\frac{1}{8}$ inches by 1 inch, whilst the centre is 1 inch square.

Full details of the mould are described and illustrated in British Standard Specification No. 12 (1947). Hind¹ has described a mould which ensures that the test piece will always fracture at the centre. Many small precautions are necessary to ensure reliable results, the more important ones being described in Hind's paper. It is essential to use only sound samples which will break centrally and be free from

¹ Hind, S. R., *Trans. Brit. Ceram. Soc.*, 29, 189, 1930.

adventitious air-blebs, laminations, etc., and are homogeneous throughout. Great care is also required in the drying of moulded test-pieces so as to avoid strains especially with fine-grained clays, which are very liable to develop fine cracks and, consequently, give low results when tested.

When testing samples in a moist or plastic state, Hind found it necessary in accurate work, to maintain the test pieces in an atmosphere of controlled (or saturated) humidity and at a constant temperature prior to (and, where practicable, during) the test. At least ten test pieces should be tested.

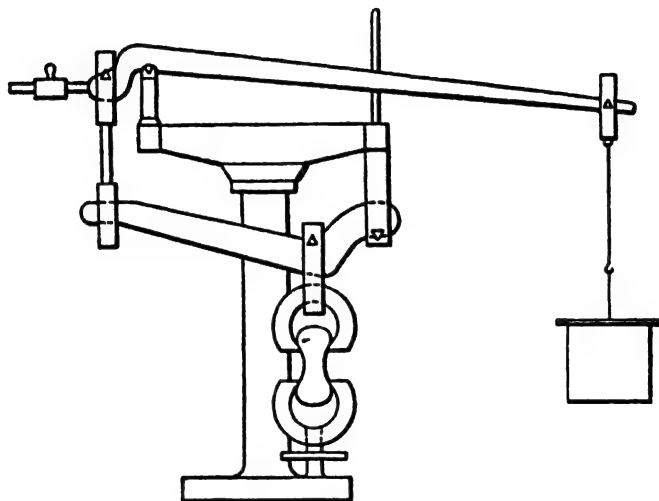


FIG. XIII.6. A TENSILE TESTING MACHINE

The test piece is placed accurately between the clips of the testing machine (Fig. XIII.6) and force is gradually applied to it—usually by shot, water, or mercury, which flows into a receptacle and so operates a series of levers, or by means of a weight sliding along a beam. The rate at which the force is applied must be the same for all pieces otherwise the results will not be comparable, the 'time factor' being very important. The usual rate is 100 lb. in twelve seconds, but for very weak specimens a much more sensitive machine and a lower rate may be employed,

When the test piece breaks, the force which has been applied is ascertained, either by weighing the shot or liquid, or by noting the position of the sliding weight, and by measuring the cross-sectional area.

Machines of slightly different pattern are available for determining tensile strengths. In some the pressure is applied hydrostatically and the point of fracture is indicated on a dial-gauge.

Various other methods have been devised for determining the tensile strength, one of which consists in measuring the length of a clay column which can be extruded through an aperture of a certain definite size before the column breaks. This test is conveniently made by placing the clay in a vertical cylinder with a $\frac{3}{8}$ -inch

aperture in the base, and a piston with screw-down motion at the top. On turning the screw slowly and regularly the paste is extruded through the aperture and hangs vertically until its weight is greater than its tensile strength, when the column breaks. The tensile strength is found by dividing the weight of the broken piece of paste by the area of the aperture through which it was extruded.

The strength of dried pottery is sometimes determined by means of a tensile test, but the transverse test, which is much simpler, is increasingly used for this purpose.

The *Extensibility* may be measured by placing the two portions of the broken test piece together and measuring the increase in its length. For this purpose, it is desirable before making the tensile test to make two small dots or thin lines on the test piece at a convenient distance apart and to measure the distance between them before and after the test. The increase in length multiplied by 100 and divided by the original length or distance between the marks will be the percentage of extensibility. Extensibility tests are preferably made on rods or cylindrical test pieces.

The **compression or crushing strength** is determined by applying a gradually-increasing pressure to a test piece of known cross-section until it either breaks or is deformed to a certain amount which is decided upon as the end-point of the test. The rate at which the pressure is applied should be constant, or the results of different tests will not be comparable. A further disadvantage of crushing tests is that unless a carefully standardised method is employed the results are not comparable, as the strength varies according to the method used for applying the pressure, the rate at which it is applied, and the shape and size of the test pieces. The most concordant results are obtained when cubical test pieces (3 in. \times 3 in. \times 3 in. for firebricks) are used, but for convenience whole or half bricks are frequently tested.

The crushing strength of bricks may be measured in several ways: The British Standard Method of determining the Compressive Strength is described in British Standard 1257 (1945); a loading rate of 2,000 lb. per sq. in. per min. is specified. The Standard Specification of the Gas and Coking Industries is that the load shall be applied in the same direction as the moulding pressure was applied during manufacture which in the case of fireclay bricks is on the 'flat', the cross-sectional area then being 9 in. \times 4½ in. = 40.5 sq. in. This method has the advantage that the bricks are measured in the position in which they are generally used, but the results are not as satisfactory as when the bricks are tested 'on end', i.e. with the pressure applied to the 4½ in. \times 3 in. face = 13½ sq. in. cross-sectional area. The crushing strength of concrete is carried out on a 6 in. cube of material.

The crushing strength is calculated by dividing the load required to cause failure by the area of cross-section of the test piece and expressing the result in lb. per sq. in., tons per sq. ft. or kg. per cm.²

Although there appears to be some relation between the strength determined on the edge face (i.e. 9 in. \times 3 in. face) to that on the flat when bricks of similar type are compared, there is no general rule because of the variations in structure. Figures published by the American Society for Testing Materials reveal that the ratio extends from 0.74 to 2.30 over a wide range of clay and shale bricks.

The American Society for Testing Materials designates that refractory bricks should be tested *on end*, i.e. the $4\frac{1}{2} \times 3$ or $2\frac{1}{2}$ face and specifies that exact parallelism in these faces must be ensured by either a shellac coat followed by a plaster coat, or by interposing 0.25 in. thick cellulose fibre wall board between the brick and press members. Furthermore the rate of loading should be standardised at 2,000 lb. per min.

As the results obtained on determining the crushing strength of a number of bricks, etc., made at the same time, and presumably of equal strength, vary considerably, it is unwise to accept the result of only one test; an average of at least twelve tests should be taken. Compression tests of plastic or dried clay should be made on twenty specimens, as the variations are often large.

The strength of refractory materials at high temperatures may be determined in two ways:

(1) The material may be heated to the desired temperature in a tubular furnace and a load applied through refractory thrust rods until the specimen fractures, or

(2) A definite load or pressure may be applied to the test piece, which is then heated under this pressure (*a*) to a fixed temperature at which the rate of deformation is measured, or (*b*) at a pre-determined rate of temperature rise until failure occurs. These tests are a measure of the *refractoriness-under-load* property which has been described on p. 775.

Transverse Tests are, for some purposes, superseded compression or crushing tests, as they can readily be made without the use of large and expensive apparatus.

In making a transverse or cross-breaking test, the test piece is supported upon two triangular 'knife-edges' and a pressure is applied by means of a third knife-edge on top of the test piece, resting on a sheet of glass or steel to prevent cutting. The pressure is increased at a pre-arranged rate, until the test piece breaks. The pressure at the moment of fracture is a measure of the strength of the test piece. The modulus of rupture (in lb. per sq. in.) may then be found from the following formula:

$$M = \frac{3Pl}{2bd^2}$$

Where *P* is the breaking load in pounds, *l* is the span in inches, and *b* and *d* are the width and depth of the test piece, respectively, in inches.

A simple but effective transverse tester for small moulded or cut specimens is shown in Fig. XIII.7. A test piece which may be of wet, dry or fired material is placed on the two lower knife-edges and pressure applied to the platform above the upper knife-edge. For specimens of low strength the breaking point can be determined by slowly running mercury or water into a beaker placed on the platform. Stronger specimens are best tested by fitting the tester between the plates of a hydraulic press and slowly applying a load until fracture occurs.

The American Society for Testing Materials requires that transverse tests should be carried out on whole bricks (C93-46), that the bearing edges should be rounded and that the loading should be applied at the rate of 200 lb. per min. The lower bearing edges are 7 in. apart and across the $4\frac{1}{2}$ in. face of the brick, and the load is applied at mid-span. At least 10 test pieces must be used.

It is most important that the test-pieces for the transverse test should be perfectly

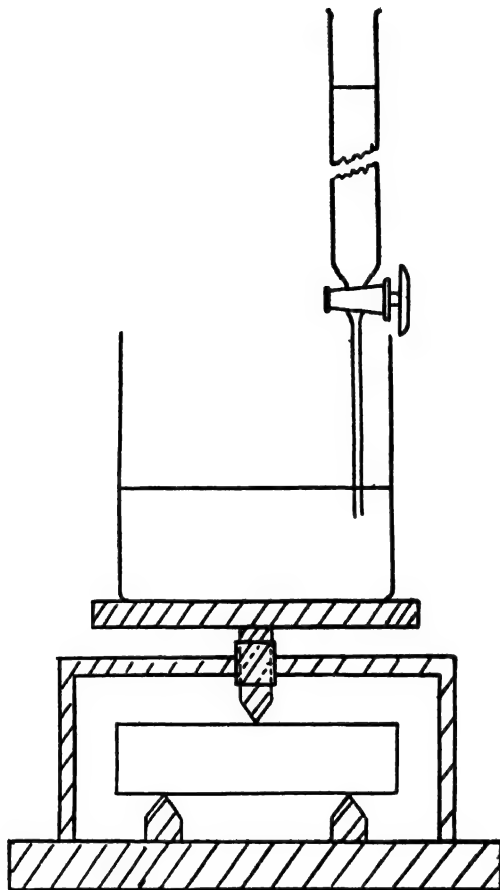


FIG. XIII.7. AN APPARATUS FOR MEASURING THE
TRANSVERSE STRENGTH OF SMALL SPECIMENS

straight and free from flaws, otherwise unreliable results may be obtained. Even with the greatest care, transverse tests give very irregular results with dried clays.

Although there is no recognised standard method for measuring the crushing strength of salt-glazed pipes, a modification of the method used for concrete pipes described in B.S.S. 556, 1955 is strongly favoured. This specifies that pipes should be placed *longitudinally* between bearers of 6 in. width with rubber packing, which shall extend the full length of the barrel of the pipe. The load is applied steadily and uniformly at a rate not exceeding 112 lb. per foot length of pipe per 10 seconds.

The A.S.T.M. test (specification 301-54) for pipes advocates either a sand-bearing method in order to secure uniformity of loading or a three-edge rubber bearing method.

Results have shown that the crushing strength of pipes is related to their internal diameter, the wall thickness and the porosity or texture of the material.

For salt-glazed and stoneware pipes, the crushing strength is usually much in excess of the minimum specification of 1350 lb. per foot of length for concrete pipes, provided that the wall thickness and water absorption are within recommended limits.

Torsion Tests. The value of torsion testing of ceramic materials has only been appreciated in recent years. The method of determining the *workability* of a plastic clay by torsional methods developed by Norton¹ is described in Chapter VIII. Roberts, *et al*², have applied the method to high temperature testing of refractory materials with great success.

The *Modulus of Elasticity* is a measure of the capacity of a body to withstand strains without becoming permanently deformed or fractured. It is an important property of many ceramic materials, particularly of glazes which may be put into considerable stress during the cooling of ware. The Modulus of Elasticity may also have an important influence on the ability of a body to withstand thermal shock (p. 865).

When a bar or block of a material is subjected to a pressure, it will be reduced or increased in length depending on whether the force is compressive or tensile. Provided that the applied force has not been too great the bar will return to its original length once the pressure has been released. The ratio of

$$\frac{\text{Unit Stress}}{\text{Unit Strain}}$$

is defined as the Modulus of Elasticity (E) and the maximum stress which a material can withstand without becoming permanently changed in shape is known as its *Elastic limit*.

The Elasticity constants can be measured by any of the conventional methods for determining the compressive, tensile or transverse strengths of materials (pp. 789-93) provided that a device for measuring the change in length of the specimen is incorporated. The usual method is to apply a pressure (P) to a test piece made in the form of a bar of known length (l) and cross-sectional area (A); the amount of strain or change in length (Δl) should then be measured. The test may be repeated at several different applied pressures until, on the removal of the applied force, the bar does not return to its original length. The *elastic limit* has then been reached. The *modulus of elasticity* is defined as Unit Stress divided by Unit Strain.

$$\text{So} \quad E = \frac{P}{A} \div \frac{\Delta l}{l} = \frac{Pl}{A \Delta l}$$

The *Modulus of Elasticity* is found by supporting a rod or bar on knife-edges and noting the weight or pressure required to bend it to a definite extent. The elasticity (E) is found from the equation:

$$E = \frac{3l^3P}{4a^3btg\alpha}$$

¹ Norton, F. H., *J. Amer. Ceram. Soc.*, 31, 236, 1948.

² See p. 796.

where a is the thickness of the test-piece, b its width, l the distance between supports, P the load or pressure and $tg\alpha$ a factor based on the angle of rise of one end of the bent test piece and on the length of the rising portion.

When a successively increasing load is applied and removed, the load which is just too great to permit the test piece to recover its normal position after the removal of the load is taken as the elastic limit. The elastic limit diminishes as the temperature of the test-pieces increases above a certain minimum. The load must be applied for a sufficient time (8 minutes or more) or erratic results will be obtained.

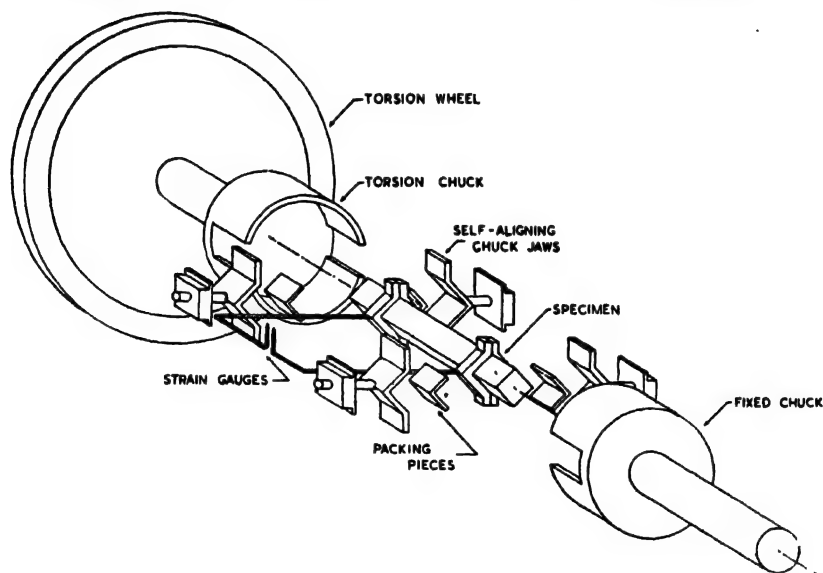


FIG. XIII.8. AN APPARATUS FOR DETERMINING THE TORSIONAL PROPERTIES OF CERAMIC MATERIALS (after Roberts)

The modulus of elasticity can be accurately determined in many other ways. Batchelor¹ has described a method for electrical porcelains and glazes using a resistance strain gauge, a sonic method has been described by Lakin,² and the torsion method used by Roberts *et al*³ to measure the Modulus of Rigidity (i.e. the Modulus when the applied pressure is shear), is extremely satisfactory. In the last mentioned, a specially-shaped test rod, cylindrical in the centre but with square end-sections is clamped at both ends in a torsion head. A load is applied at one end to exert a twisting force on the specimen, which may be surrounded and heated, if desired, by a tubular furnace, see Fig. XIII.8. Torsion tests not only permit the measurement of the progressive deformation under load, but also the elasticity of the specimen at any desired temperatures (p. 797).

¹ Batchelor, R. W., *Trans. Brit. Ceram. Soc.*, 54, 40, 1955.

² Lakin, J. R., *Trans. Brit. Ceram. Soc.*, 56, 1, 1957.

³ Roberts, A. L. and Cobb, J. W., *Trans. Brit. Ceram. Soc.*, 32, 22, 1933 and 35, 186, 1938.

The sonic method has been used by Lakin and West¹ in a study of the characteristics of refractories at high temperatures. The method depends upon the fact that solid bodies vibrate with a characteristic resonant frequency which depends on their modulus of elasticity, their density and dimensions.

A vibrator imparting a wave of known frequency is applied to one end of a brick and the position of fundamental modes determined by a gramophone crystal pick-up connected to a double beam oscillograph which also receives the signal from the vibrator. Longitudinal, torsional and flexural vibrations are set up within the brick and these can all be measured, so that, by applying suitable formulae, the coefficient of elasticity can be measured.

TABLE XIII—XIV. THE MODULUS OF ELASTICITY OF SOME CERAMIC BODIES

$E \times 10^6$		$E \times 10^6$	
Fireclays	0.5–1.0	Leadless*glaze	8
Silica bricks	0.4–0.6	Lead glaze	12
China ware	10	Glasses	10–25
Building bricks	0.7–1.2	Porcelains	8–12
Engineering bricks	3	Cordierite	7–15
Mullite bricks	1.5	Steatite	12–16
Magnesite refractories	50	Zircon porcelain	21–24
Earthenware body	5	Titania	13–16
Tile body	2		

The sonic method gives a more accurate measure of the coefficient of elasticity than does torsional measurements but, because the brick is not subjected to any strain, the development of true plastic flow cannot be observed. The development of liquid is, however, indicated by a change in the characteristic frequencies of vibration. Sonic methods of measuring the elastic constants of a ceramic material are especially valuable in their application to studies of thermal shock.

The values of the Elasticity and of the Rigidity moduli depend on two main factors: (a) the mineralogical composition; and (b) the texture, of which the former is the more important. The atomic structure of the minerals and the ease whereby movement can occur within the lattice on the application of stresses determine the coefficient of elasticity. For the most part ceramic materials have a high elasticity compared with metals; glass and glassy-bonded bodies have a higher modulus of elasticity than those which are mainly crystalline provided that the materials are of similar composition. The modulus of elasticity (also known as Young's modulus) of some ceramic bodies is given in Table XIII.XIV.

The modulus of rigidity of ceramic materials usually has a value of about two-fifths that of the modulus of elasticity.

The change in the modulus of rigidity at different temperatures in silica,² fireclay³ and basic refractories⁴ has been studied by Roberts and his co-workers. A

¹ Lakin, J. R. and West, C. S., *Trans. Brit. Ceram. Soc.*, 56, 8, 1957.

² Das, S. S. and Roberts, A. L., *Trans. Brit. Ceram. Soc.*, 48, 215, 1949.

³ Wiechula, B. A. and Roberts, A. L., *Trans. Brit. Ceram. Soc.*, 51, 173, 1952.

⁴ Chung, H. S. and Roberts, A. L., *Brit. Ceram. Soc. Meeting* (London, 1953) (as yet unpublished).

rise in modulus up to about 800° C. commonly occurs, although the cristobalite inversion point in silica refractories is marked by a sharp decrease in elasticity. The production of liquid in fireclay and basic refractories marks the beginning of a progressive decrease in modulus and this occurs at temperatures which depend on the composition of the brick. Fig. XIII.9 shows the variation with temperature of the rigidity modulus of aluminosilicate refractories. Brick A is a siliceous fireclay; the quality of fireclay as measured by the alumina content increases through bricks B, C and E, this last containing 79.50 per cent alumina; Brick D is a sillimanite refractory. The dotted line shows the changes in a silica brick under the same test conditions.

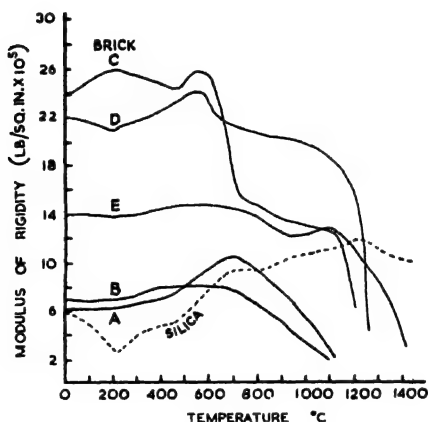


FIG. XIII.9. THE VARIATION OF THE RIGIDITY MODULUS OF SOME CERAMIC MATERIALS WITH TEMPERATURE (after Wiechula and Roberts)

The ratio of the ultimate breaking strength and the coefficient of elasticity or rigidity is an important factor in predicting the relative resistance of ceramic bodies to thermal shock; it also indicates the tendency of a glaze to craze or peel.

When tested at room temperature, most ceramic materials behave elastically until their ultimate breaking point, but at elevated temperatures the test piece 'creeps' under high pressures and permanent deformation occurs. Roberts and Wiechula recognise three different types of stress/strain curves as shown in Fig. XIII.10; (i) is of a perfectly elastic material in which the line AB represents the stress/strain relationship on both loading and unloading. *Ab* is the strain at the maximum applied stress. Curve (ii) shows an 'imperfectly elastic' deformation where the loading (AB) and recovering curves (BC) do not coincide—a 'permanent set' of AC occurs. Within the plastic range of the material, curve (iii) is obtained, which shows 'creep' or deformation (BB') whilst a fixed stress is maintained; AB again represents the stress/strain relationship during loading and B'C that during unloading.

In each case the tests were carried out by applying or removing the load in

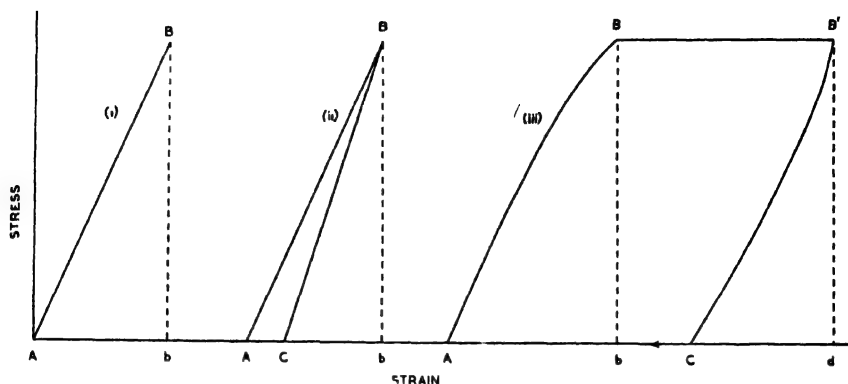


FIG. XIII.10. DIFFERENT FORMS OF STRESS/STRAIN CURVES
(i) Elastic material; (ii) imperfectly elastic material; (iii) showing plastic flow
(after Wiechula and Roberts)

fixed increments and maintaining at each value for 2 minutes. The maximum stress was maintained for 30 minutes.

Poisson's Ratio is an important elastic constant of ceramic materials; it is defined as the ratio between the decrease in width and the increase in length of a bar of material under tensile strength. It is related to the coefficients of elasticity and rigidity by the equation.

$$\mu = \frac{E}{2E_R} - 1$$

where μ = Poisson's Ratio; E = coefficient of elasticity; and E_R coefficient of rigidity.

The value of μ is relatively constant for ceramic materials, being about 0.30 for most articles made largely of clay. Glasses have a somewhat lower value and for fused silica the value is 0.15.

The Poisson's ratio decreases at higher temperatures, but not considerably unless plastic flow occurs; it is an important constant which relates to the resistance of a body to thermal stress (p. 866).

Rigidity is defined as resistance to change in shape (deformation); if the force applied is P and the amount of deformation (or strain) is a ; $P/a = E_R$ where E_R is the coefficient of rigidity. It may be measured directly but in clay-pastes it is usually determined indirectly from the amount of torsion effected in a bar of square cross-section. If the amount of twist turns the edges of the bar through an angle of φ radians then according to Hooke's law

$$E_R = \frac{P}{\varphi}$$

where E_R is the modulus of rigidity.

Deformability Tests. The deformability of ceramic materials may be determined by means of (a) a loaded rod or 'plunger' such as a Vicat needle (Fig. XIII.11), and observing either the weight required to cause the 'needle' to sink into the material

to a prescribed depth in a prescribed time, or the time required for a needle of a given weight to make an impression of a given depth. The end of the Vicat needle, which makes the impression, is usually 1 mm. square and the 'needle' weighs 300 grams. The needle may be graduated so that the depth of the impression may readily be measured. In clay pastes, it is usually allowed to make an impression 30 mm. deep. For fired articles and hard materials, a much heavier weight or, in some cases, hydraulic or other easily measurable pressure must be used to produce an impression.

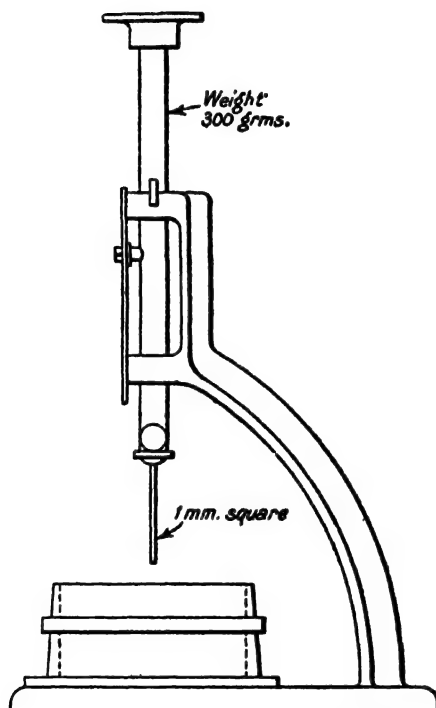


FIG. XIII.11. THE VICAT NEEDLE

(b) The weight or pressure required to reduce the height of a cylinder of the material to be tested by a prescribed amount in a given time (see also p. 484).

In both these methods, the duration of the test is important, as a small weight acting through a long period may have a deforming power equal to that of a much greater pressure acting for a shorter time.

(c) It can be shown that the diameter of the imprint (or dent) caused by a steel ball is inversely proportional to the fourth root of the Brinell Hardness so that small variations in the diameter of the imprint correspond to much larger variations of the hardness.

It is important to repeat the test a sufficient number of times on each test piece as a single test can be seriously misleading.

A spring-loaded hammer using a 10 mm. ball and applying an impact force of 50 Kg. cm. through an angle of 90° to the face of the object to be tested creates an imprint of at least 3 mm. diameter.

Impact Tests are used for determining the resistance of articles which are subjected to rough handling or are liable to be struck against other articles or to be dropped. They are also applicable to domestic table ware, electrical porcelain, and other articles in which brittleness (p. 752) is objectionable. The tensile strength of materials is sometimes determined as an indication of the resistance of articles to impact, but in this respect it is not always reliable.

An impact test devised by H. F. Staley and J. S. Hromatko¹ for testing porcelain plates consists of a pendulum 24 inches long, at the end of which is a $1\frac{1}{4}$ lb. flattened steel ball with a spherical striking surface, having a radius of $1\frac{1}{8}$ inches. The sample to be tested is placed loosely against a $\frac{5}{8}$ -inch pine board and the pendulum is allowed to swing through an angle of about 30 degrees and strike the test piece, the blows being repeated (with the pendulum moving through a greater angle at each blow) until the test-piece is broken. The impact strength is then calculated from one of the following formulae²:

$$E = HW \quad \text{or} \quad E = W(1 - L \cos A)$$

where E is the energy of impact in foot-pounds, H is the height of drop in feet $= 1 - L \cos A$, where A = the angle through which the pendulum swings, and L = the length of the arm in feet. W is the weight of the hammer in pounds.

E. Schramm³ uses a similar device for testing the resistance of china ware to chipping, but employs a pendulum about 18 inches long consisting of a $\frac{3}{8}$ -inch brass tube, the bob being a piece of $1\frac{1}{4}$ -inch steel. The piece to be tested is arranged so that the pendulum strikes its edge.

R. H. Turk⁴ has found that the most suitable type of impact machine for testing *enamels* is one able to deliver a blow equivalent to 4 foot-pounds.

Impact tests are also used for measuring the strength of floor tiles. The method recommended by F. B. O'Connor⁵ consists in supporting the tile on two knifed edges, the space between being filled level with plaster of Paris to correspond to the bedding of the tile. A hemisphere 2 inches diameter is attached to a sliding drop weighing 3 lb. and is so placed that, when the drop falls, it strikes the tile exactly in the centre. The test is carried out by first allowing the weight to fall from a height of 1 inch and then increasing the height 1 inch at a time until fracture occurs. The test is not very accurate, but is sufficiently so for practical purposes. By this method, O'Connor found the height of drop which caused fracture varied from 1.8 in. to 10 in., according to the nature of the tile.

Another important form of impact test is known as the 'rattler' test.

Rattler tests are chiefly used for testing bricks for use in roads in order to determine (a) whether the bricks are tough enough to resist the forces of impact and abrasion to which they are subjected when in use, and (b) whether the material is uniform in

¹ *J. Amer. Ceram. Soc.*, 2, 227, 1919.

² Where the angle of swing is greater than 90° $H = L(1 - \sin A)$.

³ *J. Amer. Ceram. Soc.*, 5, 136, 1922.

⁴ *Ibid.*, 13, 887, 1930.

⁵ *Trans. Amer. Ceram. Soc.*, 15, 233, 1913.

quality. The toughness is determined by the average loss of weight which the pieces to be tested undergo as the result of chipping or breaking, and the uniformity by the variation in the weight of the individual bricks or other articles after the completion of the test.

The American Society for Testing Materials has specified conditions under which the Rattler Test should be carried out (C7-52). For a full description of the complete design the reader is referred to the original paper, but a brief summary is as follows:

The standard machine is 20 in. diameter and 20 in. in length, measured inside the chamber. It is driven by trunnions at one or both ends, or by rollers underneath, but in no case should a shaft pass through the rattler chamber. The cross-section of the barrel should be a regular polygon having fourteen sides each $\frac{1}{4}$ in. apart. The heads should be composed of grey cast iron, not chilled nor case-hardened. The staves should be composed of steel plates.

All tests should be executed on charges containing but one make of material at a time. The charge should be composed of the bricks to be tested and iron abrasive material. The brick charge should consist of that number of whole bricks or blocks whose combined volume most nearly amounts to 1000 cubic in. (Ten bricks are required for the ordinary sizes on the market.)

Each brick should be marked so that it can be identified even after it has been broken. The bricks are dried and are then weighed separately before testing.

The abrasive charge consists of ten cast-iron balls, about $3\frac{1}{8}$ in. in diameter and each weighing $7\frac{1}{2}$ lb., together with sufficient cast-iron balls, each $1\frac{1}{8}$ in. diameter, to weigh 225 lb. (245-260 of these balls will be required). The total weight of the balls should be 300 lb. They should be of hard metal, as soft iron gives misleading results.

The barrel with its contents is rotated at 29.5-30.5 rev. per min. until 1800 revolutions have been made. The pieces of brick are then removed and all weighing less than 1 lb. are rejected. The residual pieces of brick are then weighed—first as a total and afterwards each brick separately. The loss in weight is calculated as a percentage of the original weight of the bricks.

This loss indicates roughly the durability of the material when in use, etc., whilst the respective loss of weight of the individual bricks used in each test indicates the uniformity, or otherwise, of the quality. Thus a charge in which the loss on the individual bricks varied greatly would indicate lack of uniformity, and in specifying the resistance to the rattler test it is customary to state that the average loss on each charge should be not more than x per cent and the maximum loss on any individual sample not more than y per cent. For paving bricks, the total loss in weight should not exceed 26 per cent and no individual brick should lose more than 30 per cent of its weight.

Freezing Tests. Some idea of the probable effect of exposure to frost may be gained by exposing the goods or materials to a 'freezing test', such as is frequently applied to building materials. In one form of this test, the article or material to be tested is dried at 100°C ., weighed, and boiled in water for thirty minutes. It is then allowed to cool and is placed in ice-cold water for one hour, after which it is placed in a refrigerator and kept at about -7°C . or 20°F . for twenty-four hours. It is then thawed and boiled again. This treatment is repeated twenty times, the loss in weight

being noted each time and expressed as a percentage of the total dry weight of the article. It was at one time supposed that there is a relationship between the porosity of burned-clay goods and their resistance to freezing, but this is not the case.

A more rapid 'freezing test' consists in immersing the article for forty-eight hours in a 15 per cent solution of sodium sulphate in water at 21° C., withdrawing it, and then placing it in a dryer at 110° C. for about seven hours. This treatment is repeated as often as may be desired. The pressure of the crystals of sodium sulphate is supposed to be similar in action to that of ice.

The freezing test of the American Society for Testing Materials consists in saturating five bricks by placing them in cold water and then heating the water to a temperature of 200° F. in thirty minutes. The soaked samples are then placed in ice water for at least one hour, after which they are weighed and then frozen in a refrigerator with all surfaces exposed at a temperature of less than 15° F. for at least five hours. The samples are then removed and placed in water at a temperature of 150°–200° F. for one hour, the freezing and thawing being repeated twenty times. After this the bricks are re-weighed and the loss in weight, as well as any visible alterations, are noted.

In another form of freezing test, the bricks or other articles, after being frozen and thawed for a prescribed number of times, are dried, and their crushing strength is then determined and compared with that of the original bricks. The effects of the freezing are then expressed in terms of the percentage loss in crushing strength.

Notwithstanding the large amount of work done both in Great Britain and in the United States, no satisfactory freezing test has yet been devised. As saturated bricks undergo a permanent expansion during freezing a measurement of this expansion may prove a better guide to the resistance of the bricks to frost than the crude methods of inspection or measuring the crushing strength of different samples before and after freezing.

Freezing tests can often be of value in revealing machine and lamination faults in extruded clay columns. A suitable length cut from a column should be placed immediately in a refrigerator unit operating at 10–15° F.; after 12 hours of such treatment the piece will show cracks or other defects if the flow of clay has been irregular in any particular direction.

Binding-power Tests. The binding power of a ceramic material may be regarded as the force which unites its individual particles together, and this is estimated from the tensile, compression or cross-breaking strengths (pp. 789–93). The determination of binding power is described in Chapter VIII.

VISCOUS AND PLASTIC FLOW AT HIGH TEMPERATURES

IN Chapter VIII, the flow properties of suspensions and the various stages in the deformation of plastic masses have been described. At high temperatures, solid bodies may behave in a similar manner and their properties in this condition are exactly paralleled by the behaviour of plastic masses, slips and suspensions.

When ceramic materials, particularly those containing clays, are heated, the fluxes present combine with other ingredients to form a liquid. Over a certain

temperature range, the body is composed of solid particles suspended in a liquid, but if a sufficiently high temperature is reached, the mass will usually become converted into a perfectly homogeneous fluid.

On cooling, some solid particles will develop, or, in glasses and glazes, associated groups form; in both cases, the mass becomes progressively more rigid and finally solidifies completely as a crystalline mass, or as a glass, or as a mixture of the two forms.

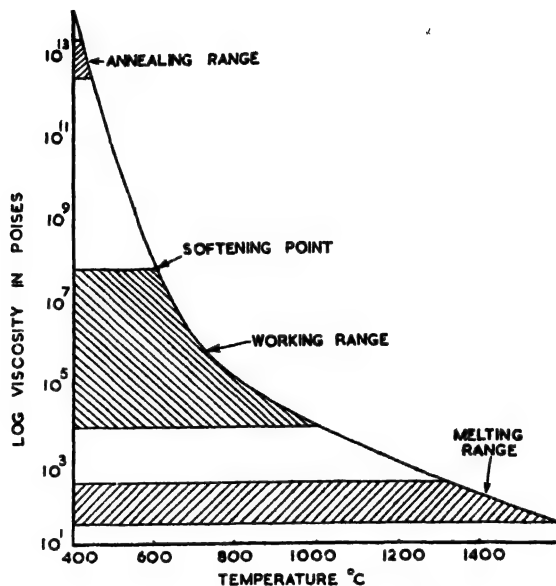


FIG. XIII.12. THE RELATIONSHIP BETWEEN THE VISCOSITY AND THE TEMPERATURE OF A GLASS

A solid mass, particularly if it is crystalline, behaves elastically, i.e. if a stress is applied, a change in shape of the body occurs, but it returns to its original shape when the stress is removed. The elasticity is maintained until the stress becomes sufficiently large to fracture the specimen.

When a proportion of liquid forms or when any glass present begins to soften, the body exhibits plastic flow (p. 461) and, when the amount of liquid is high, the flow becomes viscous.

The flow properties of clay bodies at high temperatures is well brought out by measuring the torsional properties which are described on pp. 794-98.

Glasses. The viscosity or flow properties at high temperatures of glasses and glazes is particularly important. A glassy material can be induced to flow at low temperatures, but a large pressure is required and it has to be maintained for a long period of time before any noticeable deformation occurs. At higher temperatures, less force is required to cause movement, and flow becomes progressively easier and eventually a very fluid liquid may be formed. The ratio between the applied force and the

resultant deformation is related to the viscosity (p. 448), so the effect of increasing the temperature of a glass or glaze is to decrease its viscosity.

The change of viscosity with temperature of a glass is shown in Fig. XIII.12. The important regions of the curve are:

1. *Rigid glass*, above 10^{14} poises, where little noticeable flow occurs.
2. *The Annealing range* $10^{12.5}$ – $10^{13.4}$ poises, over which internal stresses can be relieved and some degree of atomic movement is possible.
3. *The Working range*, 10^4 – $10^{7.6}$ poises, represents a condition where the glass is handleable and can be blown or rolled easily without it being too fluid. The upper limit of the working range is known as the *Softening Point*.
4. *The Melting range*, $10^{1.5}$ – $10^{2.5}$ poises, is the range of viscosity over which the glass flows readily and corresponds to its condition in the melting tank.

The temperatures over which these ranges occur differ with the composition of the glass. Alkali glasses are less viscous at a particular temperature than those containing lime and magnesia and, in general, alkali glasses have a shorter working range.

Glazes exhibit a similar behaviour to glasses but usually at a higher temperature. The most critical viscosity range in glazes is, however, between $10^{2.5}$ – $10^{4.3}$ poises,¹ because this represents the condition in which the glaze would flow with sufficient freedom to cover the surface of the body, but would be insufficiently fluid to run off the ware or to develop bubbles or pin-holes.

The viscosity of glazes and its variation with temperature is influenced by the chemical composition. Glazes rich in silica and alumina mature at higher temperatures than those with appreciable amounts of fluxes and the burning temperature must be adjusted to suit the glaze being used. Of very great importance is the maturing range of a glaze, i.e. the temperature range over which the viscosity changes from $10^{2.5}$ to $10^{4.3}$; this should be as large as possible to allow for possible temperature variations in the kilns or muffles used for burning the ware. A long maturing range can be achieved by correct adjustment of the composition and using more than one fluxing element.

¹ Bremond, P. *Bull. Soc. Franc. Ceram.*, 11, 4, 1951.

CHAPTER XIV

MISCELLANEOUS PROPERTIES OF CERAMIC MATERIALS

CERAMIC materials are of many kinds, differing in composition and property. In many cases, a product is so manufactured that one particular property is emphasised which is of value in service. The present chapter is concerned with such properties, their physical nature and their causes and effects.

COLOUR

THE colour of an object is due to the fact that when rays of light fall on it some are absorbed, whilst others are reflected, the nature of the reflected light giving the surface a characteristic colour. Thus, objects which reflect red vibrations appear to be red in colour and so on. When the light is completely absorbed the object is *black*, whilst if the light is completely reflected without change the surface will be *white*.

Colour is exhibited in various ways, so that an object may show different colours under different conditions, viz.:

1. The colour by reflected light.
2. The colour by transmitted light if the object is transparent.
3. The colour of the powder, as distinct from the mass (this is shown by drawing the mass along a piece of unglazed porcelain and examining the *streak* left on the latter).
4. The appearance of special types of colour, such as (a) *play of colours*, caused by the unequal bending of rays of light of different wavelengths giving a varicoloured effect; (b) *opalescence*, which gives a pearly or milky appearance, as shown by opals; (c) *iridescence*, or display of colours, due to inclusions of air or liquid in transparent crystals, or to peculiar irregularities in the surface of the material, as in some specimens of quartz, calcite and mica; (d) *fluorescence*, which is the ability of a material to absorb energy and then re-emit it with its wavelength altered to one in the visible part of the spectrum; and (e) *pleochroism*, a quality possessed by some transparent minerals, by which they exhibit different colours when viewed by polarised light passing through them in different directions (see also Chapter V).

Lustre is a property which may be classed with colour; it is due to the manner in which light is reflected from an object, rays of different wavelengths being reflected at different angles and so producing diffraction effects. The lustre may be (a) *metallic lustre*, such as is exhibited by many metals; (b) *vitreous* or *glassy*, as in glass, quartz, etc.; (c) *resinous*, as in resin; (d) *pearly*, as in pearls; (e) *silky*, as in satin spar; and (f) *adamantine*, as in diamond and some forms of silicon carbide.

Colour is a much more constant feature in opaque substances than in transparent ones; the latter often vary greatly in colour, because of the presence of

minute traces of other substances as impurities. Many substances have a characteristic colour, which is of value as indicating the nature of the material, e.g. iron, chromium, copper, uranium, etc.

The colours of transparent minerals are dealt with more fully in Chapter VI on 'Mineralogical Constitution'.

The colour of minerals varies considerably on account of (a) the presence of other materials; and (b) the prior history of the material, including the effect of the weather. The surface of a material or article may change colour on exposure.

The colour of most raw ceramic materials is usually a minor property and chiefly of value as an indication of the impurities present. In finished articles, it is often a very desirable property and one which contributes greatly to their beauty. In some ornamental ware and even in some utilitarian articles the colour is more important than other properties. Thus, an architect may select red bricks on account of their colour and may have to disregard the fact that the ones he chooses may not be as strong as some others. It is often easy by firing bricks at a higher temperature to make them much stronger, but, if the colour is less pleasing, they will usually be difficult to sell. Fortunately, most bricks are so much stronger than is requisite for safety that the slight loss of strength which is incurred in order to produce a more pleasing tone or colour is quite negligible for most of the purposes for which such bricks are used.

The colour of raw ceramic material does not necessarily give any indication either of its purity or the colour of the fired product. Consequently, such a material should seldom be judged solely on its colour. A dark-coloured material, such as some Devonshire ball clays, may be almost white when burned and its original colour will, in such a case, be no detriment to its usefulness. The same is true of most ceramic materials whose colour is due solely to the presence of carbonaceous matter which burns off in the kiln and is, in this way, removed. If the dark colour of the material is due to iron compounds—which are not removed by heating—it may completely spoil the material for some purposes. A light-coloured material, on the other hand, need not necessarily be of good quality, as it might contain a large proportion of colourless or light-coloured impurity, which would darken on heating or in other ways make the material unsuitable for some purposes.

Where a definite colour is desirable in the finished articles, it may be produced by various means such as:

(a) By heating the material or articles at a suitable temperature, and in a controlled atmosphere, so as to produce the desired colour. If the composition of the raw materials is suitable, no other treatment may be required. If certain colour-producing impurities are present in the raw material they may prevent the formation of the desired colour, in which case some other method must be employed. A typical example of this method of producing colour is a ferruginous clay, which, if burned at a certain temperature (depending on the clay) in an oxidising atmosphere, will produce a pleasant red colour, but if it is burned in a reducing atmosphere a dark, dull 'blue' colour is obtained, whilst when reducing and oxidising atmospheres are used alternately in the kiln, a mottled or brindled appearance is produced.

(b) A coloured substance may be introduced into the raw material, so as to

mask any undesirable colour and give the finished goods the desired tint. Thus, the addition of manganese dioxide will produce a dark brown or nearly black article, whilst cobalt compounds will give blue shades and chromium compounds green ones. The lighter the natural colour of the burned material, the greater will be the variety of colours which can be produced in this manner.

(c) If the colour of a fired material is undesirable it may be masked by coating the article with an engobe of another material which burns to a desirable colour. The engobes used for this purpose are usually white-burning clays or a mixture of such clays with flint, Cornish stone, or felspar, together with a suitable colouring agent if required, the engobe being adjusted so as to have the same shrinkage as the article to which it is applied, as well as the desired colour when burned.

The engobe is often covered with a transparent glaze, to protect it and render the article impervious to water. Sometimes, instead of a coloured engobe, a coloured glaze is used and in some faience and majolica ware a coloured glaze is used over a white engobe.

When the colour is required to be in the form of a pattern, it may be applied directly to the article or to the engobe by means of a brush, stencil, transfer, or any other convenient method. If the ware is then covered with a glaze, the method is known as *underglaze* decoration. As such colours must not be adversely affected by the firing of the glaze, only a limited range of colours is available. If, on the other hand, the colours are applied to the article after it has been glazed and fired, a much larger range of colours is available. This method is known as *on-glaze* or *over-glaze* decoration. (See p. 353.)

From the foregoing it will be seen that the most suitable method of obtaining any desired colour depends on the nature of the goods.

NATURAL SOURCES OF COLOUR

A LARGE number of ceramic materials are, when pure, perfectly white. Thus, china clay, magnesia, lime, alumina, zirconia, and silica, when quite free from impurities, burn to a white mass. Perfect whiteness is seldom attained on account of the presence of minute proportions of impurities, which have an appreciable influence on the colour of the material in which they occur. Thus, iron in small proportions is universal in its occurrence, and almost all minerals contain at least traces of it. As iron compounds have a very pronounced colour when heated to redness (except in the presence of free lime, etc. (p. 812)), iron is either a valuable accessory or a troublesome impurity, according to the conditions in which it occurs and the purpose for which the material is to be used.

The chief forms in which iron compounds occur have been outlined in Chapter VI (see p. 278).

The colours produced by iron compounds are divisible into three classes: yellows, reds, and blues. In the raw state the colour of ferric compounds varies from pale yellow to reddish brown, according to the amount present in a clay or other material, and the nature, size and distribution of the individual particles. Ferrous compounds impart a bluish or greenish tinge, which is often less noticeable

than the more pronounced colour of ferric compounds. Various modifications of the above-mentioned colours also occur, some iron compounds imparting a grey colour to the material in the raw state. Thus, most fireclays and some sandstones are grey, owing to the presence of ferrous carbonate or finely-divided iron pyrites, or, in rare cases, to iron phosphate.

Ferrous sulphate is a very troublesome impurity in clay, as it cannot easily be removed by washing, and, unless converted into an insoluble material, it often produces a bluish-green scum on the surface of the dry but unfired articles. If necessary, it can be rendered less harmful by adding a little barium carbonate to the clay.

Reds and Yellows. Some raw ceramic materials, such as bauxite, magnesite, breunnerite, laterite, and some clays, are yellowish or reddish in colour. This is commonly attributed to limonite and to haematite. The former is yellow, and the latter yellow to red, according to the state of oxidation, combination with water, and state of subdivision. They consequently impart a corresponding tint to any material in which they occur, subject to the proportion present and the influences which tend to prevent their characteristic colour being produced.¹ Ferrous and ferric oxide, either free or in combination with water or other substances, are regarded as the source of a large range of colours, varying from the lightest tawny yellow, through full yellow, orange, to a rich red colour, which resembles that so much desired in facing bricks.

In many clays, the colour cannot be due to simple iron oxide or hydroxide, because these substances are readily soluble in hydrochloric acid, which is not the case with some colouring agents in clays.

After various attempts to colour clays artificially, Goguel² has concluded that the colour of natural clays is due to a colloid, and that the colouring cannot be wholly accounted for by chemical composition, but is due to the dispersion of the colloidal matter.

In the fired or burned ware, the number of iron compounds is usually less than in the raw materials, because the hydroxides, carbonates, sulphates, sulphides, and phosphates are usually decomposed in the kiln, yielding one or more of the oxides or complex silicates. When heated to bright redness, under oxidising conditions, most iron compounds impart a reddish colour to the clay or other material containing them. This colour is commonly regarded as due to the conversion of the iron into ferric oxide, though other complex compounds are probably present, as the material is not fully bleached by boiling it with hydrochloric acid, which would dissolve ferric oxide.

The colour of raw clay may be partly destroyed by hydrochloric acid, but all the iron cannot be removed, either from the raw or fired clay. This would seem to support the idea that the iron is combined in some way with silica, or with silica and alumina, unless it is converted into a dense form of ferric oxide, which is soluble only with great difficulty in hydrochloric acid.

The colour produced by ferric oxide in fired ware is extremely variable, as

¹ It is said that there are some red clays whose colour is due to the presence of algae. The colour of such clays is deeper in the raw than in the fired state.

² *Kolloid, Z.*, 48, 305-318, 1929.

it depends upon so many factors; for this reason, the colour produced by iron compounds naturally present in the raw materials cannot usually be matched by adding any prepared materials.

Seger considered that the colour developed by iron compounds in an oxidising atmosphere depends on:

1. The amount of iron oxide or its equivalent present and the nature of the compound.
2. The composition of the fire-gases during the burning.
3. The temperature at which the material is burned.
4. The amount of other constituents.
5. The amount of vitrification which occurs.

It will usually be found that (when other conditions are constant) the colour is, to some extent, dependent on the proportion of iron present if it is in a sufficiently finely-divided condition. Thus, the presence of the equivalent of 4 per cent of ferric oxide¹ in a clay will usually impart a good deep-red colour to the burned clay. With only 3–4 per cent the colour is more usually brown or purple, whilst with less than 3 per cent the colour varies from deep buff to nearly white, the depth of colour diminishing with a decrease in the proportion of iron oxide present. It is, however, almost impossible to predict the colour of a burned clay from the proportion of ferric oxide, as there are so many other factors involved, such as the size of the particles and their previous history. In fact, Orton is very emphatic in expressing the opinion that the colour (when fired) of a red-burning clay bears no relation to its iron content, as many clays burn to the same colour, no matter whether they contain 4 or 8 per cent of ferric oxide. He further remarks that 'the distribution seems more important than the amount' and 'the conditions of firing exercise a still greater influence, so that, whilst clays low in iron never burn red, it is not possible to estimate the colour of the fired ware from the proportion of iron present'.

If a buff-coloured brick is examined under a microscope it will be seen to consist of different-coloured materials, in the form of tiny patches or dots, the colours varying from white or the yellow tint of the fired clay to brown, red, or even black spots. To the naked eye these all blend together, giving a uniform buff colour, and the more abundant the dark spots, and the nearer they are together, the deeper will be the colour; i.e. the larger the proportion of effective iron compounds present, the deeper will be the colour. The effect is similar to that produced by a large number of coloured dots on a white sheet of paper. When the sheet is held at a distance the whole surface appears to have a uniform tint. This uniformity of colour is only attained when the particles are extremely minute and very regularly distributed, and from this comparison it will readily be understood that the colour of a piece of fired material does not depend only on the proportion of iron compounds present, but also on the size of the particles and on the manner in which they are disseminated through the mass.

¹ It is customary to refer to the iron compounds in clays, etc., as though they were all present as ferric oxide. Actually, several compounds may be present as described on p. 280, so that the term 'ferric oxide' must be understood to mean the equivalent and not as necessarily implying that all the iron is in that form.

The effect of the size of the grains of iron compounds is well shown in the following: (a) If a piece of clay is soaked in a solution of a soluble iron salt, dried rapidly and burned, it will have a strong red colour; (b) if another sample of the same clay in the form of a cream or slip is mixed with a soluble iron salt, and the latter is afterwards precipitated by ammonia, and the clay is evaporated to dryness, dried and burned, it will also have a dark-red colour; (c) if powdered haematite ore is mixed with another sample of the same clay, which is then fired as before, a brownish-red colour is produced; whilst (d) if the iron oxide were in a still coarser form, the burned mixture, as a whole, would be only slightly coloured, but it would have red blotches and spots. In all these cases, the total amount of iron is the same, the difference in colour in each case being due to its form and distribution.

When a solution of an iron salt is used it permeates the whole mass and the iron is disseminated throughout the clay uniformly, except in so far as some of the solution is drawn to the surface by capillary attraction. The powdered ore is less thoroughly mixed, and, therefore, gives a less intense colour, whilst the larger grains of material merely produce spots, the remainder of the clay being scarcely coloured. It will thus be seen that to produce the characteristic colour of red-burning clays the iron compounds present must be in an extremely fine state of division and uniformly disseminated throughout the whole mass. Coarse particles merely impart a colour to a comparatively narrow zone around them, whilst the rest of the mass is unaffected. For this reason, the colour of clays cannot materially be improved by the addition of artificially prepared iron oxide, as the latter is far too coarse to give a homogeneous tint to the clay.

The iron compound in red-burning clays is in so impalpable a state, and is disseminated through the mass to such an extent, that it is almost impossible to attain a similar material by artificial means. The nearest approach to it is to add a solution of a soluble iron salt to the clay, but unless special precautions are taken (which usually result in segregating the iron and so spoiling the effect) the solution tends to accumulate on the surface of the articles during the drying stage and is brushed or rubbed off when handling the goods. In the United States, a superficial red colour is sometimes imparted to terra-cotta by spraying the dried, but unfired, ware with a 20 per cent solution of ferric chloride and afterwards firing the ware in the usual manner. A solution of ferrous sulphate appears to be useless for this purpose.

The colour produced by iron compounds on the fired ware is also greatly influenced by the conditions under which it is burned. Comparatively small changes in the composition of the fire-gases and of the atmosphere in the kiln make a great difference in the colour of the ware. The best and most brilliant red is obtained by heating the goods slowly in an atmosphere containing a large excess of free oxygen, taking care to avoid the temperature rising so rapidly that any carbonaceous matter in the clay can reduce any ferric compounds present. To some extent, the effect of a temporary reducing atmosphere may be overcome by later careful oxidation, but the resultant colour is seldom so good as if the conditions had been entirely oxidising throughout the whole period of firing. It is especially important that between 700° and 900° C. the atmosphere of the kiln should be highly oxidising, so that any of the lower forms of iron oxide may be oxidised to ferric oxide before the temperature at which they commence to fuse is attained. When once the fusion of some of the

ferrous compounds has occurred it is almost impossible to re-oxidise them so completely as to obtain a pure red colour.

The temperature to which the goods are heated is also of importance in the development of the red colour of ferric oxide; the colour produced on firing a red-burning clay becomes brighter and lighter as the temperature increases, until a maximum brilliancy is attained, usually at a temperature equivalent to Seger Cone 1a (1100° C.). At higher temperatures, partial fusion takes place and the colour is gradually darkened, the red being replaced by brown. The temperature at which the red colour is perfected depends upon the clay and varies with different materials. Some clays assume a brilliant 'terra-cotta' red colour when merely baked at 900°–1000° C., whilst others scarcely develop any red colour at such temperatures.

It has been frequently stated that 'such and such' a temperature will form a red brick and that a higher temperature will form a blue one. This is only true when other conditions are satisfied. Thus, a clay practically free from iron will not produce a red colour at any temperature unless iron oxide be added to it, and many clays which will produce a good red brick will not form a satisfactory blue one, because they either do not contain sufficient iron or because they will not stand heating to, and reduction at, the necessary temperature. Hence, the principle that the temperature regulates the colour is only true within limits; beyond these the statement does not apply.

As a general rule, the red colour begins to be replaced by brown as soon as an appreciable amount of fused or vitrified material is formed; the iron oxide then appears to combine with other minerals, yet it has never been satisfactorily explained why free ferric oxide (to which the red colour is generally considered to be due) can remain uncombined with the silica of the clay for so long at temperatures above 900° C. It may be due to the clay remaining unvitrified, and, therefore, practically inert, but this explanation cannot always apply, because the red colour is retained to perfection in a few clays which have been fully vitrified. As Orton says, 'It is truly hard to see how iron oxide can be wholly free and uncombined in a vitrified mass of such perfection', though it appears to be so, and the fact that, on further heating, these clays blacken and iron silicates are then formed, makes it appear probable that the combination of the iron compounds with the silica of the clay can only result in the loss of their red colour and in the production of black (technically 'blue') wares due to the formation of ferrous silicates. The true cause of the inertness of the so-called free ferric oxide in red-burning bricks has not been found.

Effect of Minerals on Red Colour. The presence of various materials in a clay has an important influence on the colour developed by iron compounds. If a large proportion of colourless matter, such as sand, etc., is present, especially if it is somewhat coarse, the colour developed by the iron compounds is not so intense as might be expected from the percentage of iron oxide shown by analysis. The difference may be partly due to adsorption phenomena, as the colouring matter cannot so readily tint grains of sand and other impervious minerals as those of the more porous clay.

The red colour produced by iron compounds is also modified by free alumina, Seger having found the following relations between the composition and colour in various clays:

<i>Character of clay</i>	<i>Colour after burning</i>
High in alumina and low in iron	White, or nearly so
High in alumina and moderate in iron	Pale yellow to pale buff
Low in alumina and high in iron	Red
Low in alumina and high in iron and lime	Cream or yellow

According to Seger, some clays containing iron compounds have, when burned, a yellowish colour due to the interaction between the iron compounds and the alumina, the latter decolorising the iron in the same way as lime (*infra*), though to a much smaller extent, as lime is a more powerful base. His experiments suggest that the best red-burning clays contain two or three times as much alumina as iron oxide. This influence of alumina is not admitted by Orton,¹ who denies the bleaching action of alumina upon iron oxide, because he has found buff-burning clays of practically the same colour, the composition of which fluctuates between 40 per cent of alumina and 0.5 per cent of iron oxide, and 15 per cent of alumina and 2.5 per cent of iron oxide. L. A. Keane,² on the contrary, has found that alumina sometimes aids in the distribution of the iron oxide through the mass and also prevents the proper formation of the red colour by ferric oxide.

The presence of some other oxides, such as *lime*, *magnesia* and *alkalies*, is also adverse to the production of a good red colour by iron compounds, as they tend to cause the clay to fuse and so darken the red colour and form an unpleasant shade of brown. This is supposed to be due to the iron oxide combining with the fused material forming iron silicates, which do not possess the red colour of the free ferric oxide.

Lime, when present in a red-burning clay, will combine with the iron present to form a white or cream-coloured double silicate. The white Suffolk bricks are produced by this means. Seger has found that the whitest products are obtained when the proportion of lime is equal to not less than two and preferably four times that of the iron expressed as ferric oxide. In practice, a large proportion of lime or chalk is usually necessary.

The decolorising effect of lime cannot occur when sufficient sulphurous fumes are present in the kiln gases, as these combine more readily with the lime than the iron does and form calcium sulphate, which produces a scum on the surface of the goods. The inside of the articles, however, which are not affected by the sulphurous gases, are decolorised in the normal manner. This effect of sulphurous gases is well shown by some tests made by Aron, who found that the red parts of bricks contained 8.49 per cent of sulphates, whilst the decolorised parts contained only 0.6 per cent.

Maw has found that the presence of 5 per cent of *magnesia* prevented the production of the red colour in various clays which he examined.

Lime and magnesia each neutralise the colour of iron compounds to the extent of about half their weight, so that a clay containing 4 per cent of iron oxide and 6 per cent of magnesia or lime will, when burned, have a colour such as would be produced were lime and magnesia absent and only 1 per cent of iron oxide were present.

The effect of *fine fluxes* in destroying the red colour produced by iron is shown by the fact that coarse, sandy clays retain their red colour when heated to a higher

¹ *Trans. Amer. Ceram. Soc.*, 5, 389, 1903.

² *J. Phys. Chem.*, 20, 724-760, 1916.

temperature than fine-grained clays, as the latter contain a larger proportion of fluxes which fuse at a lower temperature and so cause the loss of colour (due to the formation of iron silicates) at a lower temperature than would otherwise be the case. Thus, E. Orton found that a sandy clay retained a strong red colour up to Cone 8, but another red-burning clay containing a larger proportion of actual clay attained a maximum red colour at about Cone 1. Above this temperature, the colour became dark brown and was spoilt by the formation of silicates. Ries has also confirmed this effect of fluxes.

The red colour is best produced in the absence of all other impurities than iron oxide, and this should occur in an extremely finely divided condition, disseminated uniformly through the clay. If necessary, the clay may be purified (Chapter VIII) so as to improve the red colour produced by the iron oxide present.

Blues and Blacks. The blue or black produced in fired goods is usually due to the presence of ferric sulphide, ferrous compounds, or to magnetic iron oxide, each of which can combine with silica at a red heat to form a dark, fusible, slag-like mass, which is readily absorbed by the porous, fired clay to which it imparts its colour. Sometimes it forms crystals of *fayalite* (FeSiO_3).

Ferric sulphide (pyrite) produces isolated black spots in the fired ware. These are due to the ferric sulphide (FeS_2) losing half its sulphur at a temperature of about 800°C . and to the resulting ferrous sulphide (FeS) combining with any free silica present and forming a dark fusible ferrous silicate. If the particles of sulphide are very small, they produce isolated black spots, but if they are larger or very numerous they form blotches or patches of a dark slag-like material which may be $\frac{1}{2}$ in. or more in diameter and render the ware unsightly.

The iron in fireclays appears to be largely in the form of pyrites or nodular ironstones, and those clays are consequently buff or light yellow when burned, with small spots or patches of dark slag disseminated through the mass in proportion to the amount present. These iron-bearing minerals never occur in such fine grains as to give an even red colour to the goods in which they occur, but usually produce dark spots in the ware.

Magnetic oxide of iron (Fe_3O_4) is black and is produced by the partial reduction of ferric oxide, under conditions which do not permit its complete reduction to ferrous oxide. It occurs in some raw clays and in some buff bricks, in the firing of which there has been a slight reducing action. It is similar in action to a mixture of ferrous and ferric oxides.

The *ferrous compound* naturally occurring in raw ceramic materials is chiefly ferrous carbonate, with small proportions of ferrous hydroxide or oxide. When heated in the absence of air, all these substances form ferrous oxide (FeO), and may, without serious risk of error, be considered as though they consisted wholly of ferrous oxide.

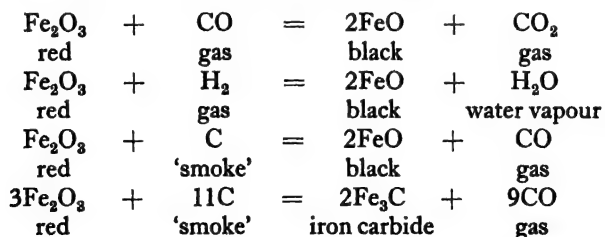
Ferrous carbonate is often difficult to oxidise, even in a suitable atmosphere, and so does not always give a good red colour. It has a tendency to granulate and to produce black or dark brown spots, but if the clay is finely ground and the kiln is skilfully managed a fairly good red colour may be produced.

Ferrous oxide is the lowest oxide of iron and has a bluish colour. It does not usually occur in the free state, but is produced in firing under reducing conditions,

and then, on account of its low fusing point, it readily combines with silica, forming fusible ferrous silicates, which produce a blue or blue-black colour in the fired goods. The conditions under which ferrous oxide is produced are determined by the nature of the clay, the proportion of iron compounds present and the manner in which the clay is heated. The ferrous oxide probably exists as such for only a few moments; it either combines almost immediately with any adjacent clay or silica, or if this is impossible it usually becomes oxidised to ferric oxide during the cooling of the material in the kiln.

Ferrous oxide is produced by the reduction of red ferric oxide by carbon monoxide and other reducing agents in the gases used for heating the material. If the reduced oxide is sufficiently abundant and properly distributed it forms a ferrous silicate and so produces the dark fusible material to which Staffordshire blue bricks owe their characteristic appearance. The reduction process is known as 'blueing'; it may be produced intentionally in a variety of ways, in some of which the use of free carbon, hydrocarbon, carbon monoxide, or possibly hydrogen, is required. These may be produced by the gases from the coal used in heating the kilns, or by the use of heavy residuum tar, juniper wood or other hydrocarbons. By whatever means it is produced, its action is to reduce the iron compounds present in the clay from the ferric to the ferrous state, in which they can combine readily with the silica and heated clay, forming complex silicates of a slag-like character. These molten slags rapidly fill the pores of the material, so that when the 'blueing' is complete the mass is no longer porous, but consists of a vitreous material, the pores of which have been completely filled with a tough glass or slag, the whole forming a solid mass of great strength and toughness.

The manner in which the reduction takes place does not seem capable of any simple expression, but apparently the first stage consists in the production of magnetic oxide and this is later reduced to ferrous oxide or silicate, or possibly iron carbide (Fe_3C) or carbonyl (FeCO) may be formed, at any rate in part. A considerable amount of free carbon is also deposited in the pores of the clay when oils, or certain special materials, are being used to produce the blueing. The action of these reducing agents may be represented by four equations:



Under the usual conditions of working, the gases which effect the burning contain an excess of carbon monoxide, and if there is insufficient air to burn the gas to carbon dioxide, the burning gases will draw supplies of oxygen from the higher compounds of iron in the goods, thus converting them into the lower or ferrous state.

In order to effect the complete blueing of bricks or tiles, the gas should be as clean as possible, as if it is charged with large quantities of soot the outside pores

may be filled with deposited material which prevents the interior of the goods from being properly blued and the latter, if broken, will not be 'blue throughout'. The articles must also be sufficiently porous to allow the reducing gases to enter and effect the reduction.

Another reaction which may aid in the blueing is the formation of magnetic oxide of iron by the partial reduction of red ferric oxide (p. 813) and the subsequent dissociation of this into ferric and ferrous oxides. At a sufficiently high temperature, ferric oxide can also dissociate, evolving an atom of oxygen from each of its molecules and forming the magnetic oxide



The blueing is usually effected by the reduction of the ferric oxide, but if this fails the kiln may be heated more intensely with as little admission of air as possible, in order to decompose any remaining red ferric oxide and convert it into the black magnetic oxide which subsequently decomposes and forms fusible silicate.

Some of the magnetic oxide may also remain in the free state, in which case, as it is black, it adds to the dark colour desired.

Although the process of blueing may be explained as due solely to the reduction of ferric compounds in the clay, such an explanation cannot be complete, because the colours of synthetic ferrous silicates are quite different from that produced in bricks by firing in a reducing atmosphere; the latter are probably coloured by carbonaceous matter (from the smoke produced by the fuel) as well as by the ferrous silicates, though carbonaceous matter alone, in the absence of iron, produces black, but not 'blue' ware. If the temperature at which the blueing has been effected is not too high, the red colour of the ware can be restored by reburning in an oxidising atmosphere; this reversal of colour may be repeated indefinitely if the temperature is carefully controlled and seems to suggest that the iron in blue bricks may be combined with some form or forms of alumino-silicate, in which its state may readily be changed from ferrous to ferric, or *vice versa*. On heating to higher temperatures, this compound appears to be decomposed and irreversible silicates are formed.

The effect of the size and distribution of the particles of ferrous iron compounds appears to be as important as in the production of a red colour by ferric compounds. A uniform 'blue' colour is produced only when the iron compounds are in an extremely fine state of division and are uniformly disseminated through the material. When they occur in large pieces they form blotches of a blue-black material similar to those produced by coarse particles of ferric sulphide (pyrite).

The effect of impurities in the clay (other than iron compounds) in the production of a 'blue' colour has not been adequately studied, but so far as can be ascertained, lime, magnesia, and the alkalis do not affect the production of a blue colour unless present in such large proportions as to render the clay too fusible to enable it to keep its shape at the temperature required for blueing.

Black ware and the black discoloration and cores are usually produced by ferrous and magnetic oxides,¹ either alone or with unburnt carbon and are due to a deficiency of air when the goods are at a temperature between 500° and 900° C., particularly if

¹ A mixture of cobalt, manganese and chromium oxides, with iron oxide is also used for black ware (see p. 821).

the temperature rises very rapidly, so that the carbonaceous matter is not burned out before vitrification commences at the surface of the goods and prevents the proper oxidation of the carbonaceous matter in the interior. Such a state of affairs is due to unskilled management of the kiln and is considered fully in the *Clayworkers' Handbook* (Griffin), by A. B. Searle.

The colours produced by iron compounds do not always belong to one or other of the three classes mentioned on p. 807. In some cases, mixtures of different colours are obtained. Thus, if a clay containing sufficient iron oxide is burned in an atmosphere which is alternately oxidising and reducing, such as may be caused by the presence of an excess of air at some periods in the burning and a deficiency of air at other periods, a variegated colour or 'brindled' effect may be produced. In the oxidising atmosphere, the iron compounds produce a red colour, but when the atmosphere becomes reducing a part of the iron compounds may be changed into the ferrous state, this giving a blue colour. If the alternations are fairly rapid, the reduction or oxidation cannot be completed so that the resultant products contain some iron compounds in the reduced and some in the fully oxidised condition, thus producing a mottled appearance. When this effect is produced deliberately, it is known as 'flashing'; it is frequently employed in the production of certain classes of facing bricks and other goods and with small kilns worked at moderate temperatures it is not difficult to obtain very pleasing effects. The difficulties increase rapidly, however, with an increase in the temperature and size of the kilns. The great point is to secure the complete oxidation of the carbon in the clay (if any be present) at a sufficiently low temperature, so that it cannot combine and reduce the iron in the clay to such an extent that subsequent oxidation becomes impossible. Too rapid heating of the kiln when it is just below 900° C. is also the cause of thousands of facing bricks being spoiled, because the carbonaceous matter they contain is decomposed and 'set' in such a way that it cannot afterwards be burnt out without spoiling the colour of the goods. Whilst this process of flashing is often intentional, to secure certain effects, it sometimes occurs when it is not wanted and is then regarded as a defect. In such cases, it is generally due to lack of skill in firing the kiln and especially to putting the fuel in the firebox in too large quantities at too long intervals, instead of smaller charges supplied more frequently.

Carbonaceous Matter. Next to iron, probably the most important colouring agent in raw materials is carbonaceous matter.

The grey, bluish black, red, and other tints of unburned clay and other minerals, although usually due to mineral impurities, are, in some cases, of vegetable origin, the composition of the colouring matters being often imperfectly understood. It is not improbable that it is partly due to finely-divided coal, or to some dye-like material formed—like the brown colouring matter of peat—by the decomposition of vegetable matter.

These organic colouring matters are destroyed on firing, so that a clay may be strongly coloured in the raw state and yet burn perfectly white.

Ball clays are typical examples of materials containing a large amount of organic colouring matter. Some of them are dark blue or even black, but when heated to redness in an oxidising atmosphere they become almost white or pale buff, according to the other impurities present. Most natural clays, and many refractory materials,

are coloured to some extent by carbonaceous matter. Further information on the colouring effect of carbonaceous matter will be found in Chapter VI.

Use is sometimes made of the fact that carbonaceous matter burns out in the firing, by mixing special bodies and pastes with some strong aniline dye, such as methylene blue, which will burn off in the kiln, but which imparts a distinctive colour to the material whilst in the raw or dried condition, though it does not affect the fired goods. By this means, the unfired bodies may be identified by the colour.

COLOURS OF RAW CLAYS

THE colour of a raw material is no criterion as to its colour when burned. A clay which is grey or yellow when freshly dug may, on burning, give a good red colour, equally as well as a clay which is a red or brown when first found. This is largely due to the fact that the colours of natural clays are largely organic in character and so are destroyed when the clays are heated. It is also due to the fact that the iron compounds in clays are usually very pale in colour, or are almost colourless and only develop their full red or blue colour when the clays are fired.

The two principal colouring materials in clays in the raw state are iron oxide and carbonaceous matter.

Variations in colour in different strata do not necessarily indicate any appreciable difference in composition, nor is the colour of a deposit necessarily a reliable guide to the purity of the material, as the amount of impurity producing a certain colour may be very small in comparison with the colour it produces.

The colour of a ceramic material may vary in different parts of the same bed on account of its proximity to other strata, or for other reasons. Thus, if a clay bed lies immediately below lignite, the portion in contact with the carbonaceous bed may be bleached by the reduction of the iron compounds, whilst the lower portion of the clay bed may be quite dark in colour.

The exposed surface of light-coloured beds is sometimes brown, as a result of the oxidation of the iron compounds in the clay, and if a section is examined it may be found that the colour gradually becomes lighter and lighter, with increasing depth. The extent of coloration by oxidation is largely dependent upon the permeability of the material. Thus, an open material would be stained to a greater extent than a close-grained one, whilst the presence or absence of fissures and cracks would also affect the resultant colour.

Very few clays are pure white in the raw state, as the presence of only a very minute proportion of impurity may affect the colour to a considerable degree.

Kaolin and **china clay**, when reasonably pure, should be white or pale cream in colour, but the tint varies irregularly with the amount of impurity present. Some less pure primary clays have a greyish tint on account of carbonaceous matter present, whilst others are slightly brown as a result of the presence of small proportions of peat or iron compounds. Some china clays are tinted pale blue on account of bright blue needle-shaped crystals of tourmaline present in them. China clay varies in whiteness to a considerable extent, according to the amount of moisture it contains. If a sample is dipped in water it may become grey or bluish in colour;

some china clays when so treated have a distinct yellow tint, though they are practically pure white when dry.

Ball clays may be black, blue, brown, or white. The black is due to the presence of carbonaceous matter, some ball clays containing as much as 10 per cent of carbon in the form of lignite or other organic matter. Many ball clays contain 3–4 per cent of carbon, which is equivalent to a much larger proportion of carbonaceous matter.

Some of the purest varieties of ball clays in South Devon are white, but the variety known as 'white clay' varies in colour from snow white to a pale straw tint. Other ball clays vary in colour in different beds, through grey, blue, brown, or chocolate colour to a deep black. The colours of the Dorset ball clays are equally variable. In each case, the greater part of the colour is due to carbonaceous matter, though some clays are tinted with iron oxide and hydroxide. If this is separated by a washing process, it usually produces a good quality of ochre.

Many of the so-called 'blue' ball clays (including some of the best kinds of ball clays) are yellowish or grey in colour when freshly obtained, but when exposed for some time they become tinged with brown, though even after prolonged exposure they do not become much darker in colour than sometimes they turn rather paler. Some blue ball clays are spotted or mottled, but this does not affect their colour when burned.

Ivory ball clays are creamy, drab or blue-grey in colour and are very similar to blue ball clays except that they contain more iron. When exposed to the weather, ivory ball clays differ from the blue variety in becoming 'rusty', due to the oxidation of the iron salts present.

Surface clays and **brick earths** are very variable in colour according to the impurities they contain. The commonest are yellow, brown and blue; these colours are due to the presence of iron compounds. Thus, a yellow colour in clays may be due to the presence of ferric hydroxide (limonite, $\text{Fe}_2(\text{OH})_6$) or to the colour of the iron being rendered paler by the action of lime compounds disseminated through the clay. The green colour of some raw clays may be due to the presence of iron silicates, such as glauconite or chlorites.

Many stoneware clays, when freshly dug, are grey, yellowish, or blue, the blue shade being due partly to the presence of ferrous compounds. Silt, warp, and similar beds are often of a light chocolate colour. The pocket clays of Derbyshire and Staffordshire vary very considerably in colour. Some are quite white, whilst others are yellow, red, purple, mottled, and even black. The whitest of these clays are not necessarily the purest, but owe their appearance to the presence of minute flakes of mica which make the material white and glistening.

Fireclays and some **shales** are a grey or slightly bluish colour on account of the presence of organic matter which occurs in minute particles disseminated through them. Some fireclays are quite black and have bright cleavage faces. Near the surface, a clay may be nearly white with a slight tinge or mottling of red, grey, or yellow, but patches of strongly ochre-coloured material often occur at a slightly greater depth. Some shales, after being dug and exposed to the action of the weather, turn yellow or brown as a result of the oxidation of the iron compounds present.

Some clays are naturally mottled on account of the irregular distribution of impurities in them; the 'mottling' usually disappears during the firing.

COLOURS OF BURNED CLAYS

As previously explained, the colour of a burned material, and particularly of a burned clay, has no constant connection with its colour before firing, though in some cases it is possible to predict roughly what will be the colour.

The colour of burned clay depends chiefly, but not wholly, on the proportion of iron present. Clays which contain only a very small proportion of iron will be white or pale cream when fired, and, as the proportion of iron oxide increases, the colour will vary from primrose yellow through buff, red, brown, grey, blue, or black, whilst in some cases, it may be mottled on account of the irregular distribution of the iron compounds present.

Table XIV.I shows the colours which may be expected from clays of various colours in the raw state when burned in a clean atmosphere free from smoke, though, as already explained, it is impossible to predict the colour with certainty.

TABLE XIV—I. COLOURS OF RAW AND BURNED CLAYS

<i>Colour of Raw Clay</i>	<i>Probable Colour of Burned Clay</i>
Red	Red or brown
Deep yellow	Buff, red or brown
Chocolate	Red or reddish brown
White	White or yellowish white
Grey or black	Red, buff or white
Green	Red
Red, yellow, or grey (calcareous)	Red at first, then cream, yellow, buff, or white, and greenish yellow when becoming viscous

Kaolin and **china clay**, when pure, are perfectly white after burning; if they contain a very minute proportion of iron compounds, the burned clay has a pinkish or reddish tinge. For some purposes, a slight discoloration is not of great importance, as it does not appreciably affect the refractoriness.

Ball clays are white or cream in colour when burned. Ivory ball clays generally become a yellowish buff when burned, as they contain a larger proportion of iron oxide than the purer varieties of ball clay.

Brick earths, when burned, vary considerably in colour, according to the conditions mentioned on p. 809. *Red-burning clays* owe their colour to the presence of iron compounds and the absence of more than very small proportions of other bases. Some of these clays are renowned for the beautiful red colour which they assume when burned. Amongst these are the Ruabon clay, the 'red marls' of Staffordshire and Leicestershire, and the red-burning clays of Shropshire, Lancashire and North Wales.

Other good red-burning clays occur in Hampshire, Berkshire, Nottinghamshire, Leicestershire, Lancashire and Yorkshire. Good colours may be obtained with many other clays, but the ones mentioned are usually the most pleasing.

Bagshot clays are well known for the excellent red colour they produce, whilst the Oxford clays are somewhat lighter. The Midland and Western clays give varying shades, most of them burning to a red colour. The majority of surface clays are red

when fired, though there are some exceptions. Many shales burn to a red colour, though others are much lighter when fired.

The value of some red-burning clays is dependent on the absence of scum, specks, blisters, etc., which sometimes accompany and spoil what would otherwise be a good colour. Black, white, or cane-coloured spots also occur and spoil the appearance of some red-burning clays. The best clays give a good red of uniform character over the whole brick, but some architects and builders prefer bricks, etc., with an irregular, spotted, or mottled appearance due to the presence of iron compounds in a coarser state than that which produces bricks of a uniform red tone. Thus, some of the Humber silt produces bricks of very variable colour, all shades from dark purple to dirty white, though blue, red, and yellow are sometimes found in

TABLE XIV—II. COLOUR OF ROOFING TILES

<i>Colour</i>	<i>Cone</i>	<i>Temperature, ° C.</i>
Immature and high red colours	Up to 06a	Up to 980
Commercial red	05a-1a	1000-1100
Overmature red or brown with body still sound	2a-4a	1120-1160
Blue or black colours with failure of body	5a and over	1180 and over

the same brick. When these varied colours form a pleasing combination the clays may be valuable, but, as the tints cannot usually be regulated, the risk of producing unsaleable goods is often very great. Facing bricks, terra-cotta, floor tiles, roofing tiles and some coarse pottery are dependent on the production of a pleasing red colour when fired at a moderate temperature and the value of the clays used for making these articles depends on the quality of the red colour produced. If too high a temperature is required to develop the colour, the production of the goods will be costly and in most cases, the colour will not be very pleasing.

E. Orton¹ has stated that a good red-burning clay should have a yellow, red, or salmon colour at 900° C. and should attain maximum brilliance at about 1100° C. Many of the bricks and tiles of the Midlands and North of England are usually burned at a higher temperature than is required to produce the most pleasing tint; this is done to secure increased strength and a less permeable product which will remain 'clean' longer than a very porous brick. W. G. Worcester² has stated that many good roofing tile clays give the following colours at the temperatures shown in Table XIV.II:

Many manufacturers, unfortunately, place the colour of their goods before anything else and will even sacrifice durability in order to obtain a certain 'saleable tint'. There is much excuse for their doing so when there is a ready demand for their goods, but it is unfortunate all the same. The result of this is that many unglazed articles have been very imperfectly 'baked' in the kiln, the heat being merely sufficient to develop the required colour and no more. Such articles may last a long time under favourable circumstances, but they cannot compare for durability with those which have been heated to the point of incipient vitrification, where the

¹ *Trans. Amer. Ceram. Soc.*, 5, 413-415, 1903.

² *Geol. Survey of Ohio, Bull.*, 11, p. 102.

particles of clay are bound together by the molten particles of the more fusible constituents.

Blue and black bricks and tiles are usually formed by burning clays containing a sufficient proportion of iron compounds in a reducing atmosphere though they may also be due to the presence of manganese dioxide occurring naturally in a clay or to a mixture of cobalt and manganese oxides added thereto.

Black bricks are sometimes produced by the deposition of carbon in the pores of articles, the particles being subsequently fixed by the fusible matter on the surface of goods. Crucibles, etc., composed of a mixture of clay and graphite are also black.

A purple colour on bricks and tiles is sometimes a result of the partial reduction or of the decomposition by overheating of red ferric oxide in the clay. Some clays yield this colour more readily than others, but it can sometimes be produced by adding a little manganese dioxide, coke-dust, or even ashes, to a clay, though no artificial mixture is quite reliable. It is usually found that only a small proportion of the goods fired in a kiln possess the desired purple colour; the others may be blue, brindled, or red.

A mottled or irregular colour may be due partly to the composition of the material and partly to the method of firing. With materials containing much combustible matter—whether in the form of cinders added under the name of 'soil', or of material naturally present as 'organic vegetable matter' or 'oil shale'—a certain amount of irregularity of colour is practically unavoidable unless the means used to mix the material are so complete and the combustible matter is so fine, that a perfect distribution can be effected. In most cases, in the parts of the goods where the combustible matter is most prevalent, it will burn without a sufficient quantity of air and will consequently take the oxygen from any iron compound in the immediate vicinity, provided that such oxygen is available. This will necessarily lead to a change of colour in certain portions of the goods, for the reduced iron compound will be bluish or even black, whilst the fully oxidised one is red. This kind of irregularity in colouring can only be avoided by so fine a grinding and so thorough a distribution of the combustible matter as is quite unattainable in commerce, and it is a fortunate thing that many of the irregular colours produced are so effective when the bricks, tiles, etc., are in use, that they are actually sought for by architects and others.

In the absence of sufficient combustible matter in the goods, a mottled or irregular appearance may be produced by alternate reducing and oxidising atmospheres in the kiln. By repeatedly changing the nature of the atmosphere the iron compounds are partly reduced and partly oxidised, this giving a mottled or flashed appearance which is highly prized in goods made for some purposes.

The speckled bricks so valued in America are made of light yellow clays containing manganese dioxide, which causes small black spots to appear on the surface of the bricks.

Further information on mottling and variegated colours will be found on p. 829. **Whiteware.** The term 'white' is often used very loosely in clayworking, and is used to include all shades from a true white to a distinct cream or even a pale yellow colour.

White goods, when made of clay, are usually formed of white-burning clays, etc., of great purity, or of a mixture of china clay, ball-clay, flint, Cornish stone,

felspar, etc. When such clays or mixtures are too costly to be used to form the whole article, the latter may be made of a cheaper clay which is buff or red when burned, but is made to appear white by covering it with a white-burning mixture, such as that just mentioned. This process is known as engobing or bodying.

Some clays containing a large amount of calcium carbonate, as well as a considerable proportion of iron compounds, are quite white when burned. They are used for making white bricks in Cambridgeshire, Norfolk and Suffolk and to a smaller extent in Sussex. They owe their whiteness to the combination of the iron with the lime, silica, and alumina in the clay.

Gault clays (which sometimes contain as much as 35 per cent of calcium carbonate) produce nearly white bricks. When the proportion of calcium carbonate is high, Gault clays are best mixed with sufficient red clay of another formation so as to reduce the proportion of calcium carbonate in the mixture to not more than 25 per cent.

Some of the white bricks in Suffolk are made by mixing a red-burning clay with a sufficiently large quantity of chalk in a wash-mill, and some of the red surface clays of some parts of Yorkshire are made to yield a whitish brick by mixing them with magnesian lime (or dolomite) in a slaked conditions. These clays are naturally wet when dug and the lime is valuable, as it absorbs the moisture in the clay without the necessity of drying it before grinding.

The effect of minute proportions of colouring agents naturally present as impurities in white-burning materials and also the effect of the atmosphere in the kiln, are clearly shown in Table XIV.III, due to W. H. Yates and H. Ellam.¹

It may be explained that the *biscuit ware* is the unglazed material; the *glost ware* is the biscuit ware which has been covered with a transparent, colourless glaze and refired at a lower temperature; the results shown in the last column were obtained by reheating the ware at about 900°–1000° C. among articles which had been decorated with overglaze colours which required to be fired at this temperature.

When bone china ware is fired under reducing conditions it may assume a bluish shade, which is attributed by Moore and Mellor to the partial dissociation of the bone ash (calcium phosphate) and the resulting formation of ferrous phosphate. A larger proportion of ferrous phosphate is formed, according to J. W. Mellor,² when the china ware is deficient in Cornish stone or contains too large a proportion of clay. On the other hand, the higher the proportion of alkali the less is the liability to form ferrous phosphate.

It is extremely difficult to produce perfectly white goods, as even minute amounts of iron oxide have a strong power of discoloration. The latter may be minimised when it only occurs to a very small extent by (a) the use of a reducing fire during part of the period of burning, or (b) by adding a suitable colouring agent to neutralise the colour and so produce a pure white ware. Thus, the addition of a minute proportion of cobalt oxide satisfactorily corrects a faint yellow colour in the wares. This is due to the fact that yellow and blue colours are complementary and neutralise each other, producing an almost perfect white, if the total amount of colour is not too large, otherwise a green colour is produced. The action is the same

¹ *Trans. Eng. Ceram. Soc.*, 17, 120, 1917–18.

² *Trans. Eng. Ceram. Soc.*, 18, 497, 1918–19.

as in the use of 'blue' in laundry work. The prepared cobalt oxide may be added either to the body or to the engobe or glaze placed upon it. The latter is the cheaper, but the former gives the most dependable results, the cobalt being added either in the form of a very fine powder or of a solution of cobalt chloride (or sulphate) in water. If the solid material is used, it must be ground extremely fine or it will produce minute blue spots instead of making the ware white. Instead of adding the

TABLE XIV—III. EFFECT OF COMPOSITION AND FIRING ON COLOUR OF BONE CHINA WARE

<i>Per cent of Ingredients</i>			<i>Colour of Biscuit</i>	<i>Colour of Glaze</i>	<i>Colour after passing through Enamel Kiln</i>
<i>China Clay</i>	<i>Bone Ash</i>	<i>Cornish Stone</i>			
100	0	0	Cream	Cream	Cream
80	20	0	Brown	Slightly paler	Brown increased
80	0	20	Yellow	Shade lighter	Brown
60	40	0	Pink	Red brown	Red
60	20	20	Light brown	Dirty brown	Slight, where glazed thick
60	0	40	Cream	Yellow	Brown
40	60	0	Green	Pale green	Still paler
40	40	20	Pale green	Green much increased	Brown in patches
40	20	40	Yellow	Yellow	Yellow
40	0	60	Slight brown	Slight brown	Slight brown
20	80	0	Brown	Shade lighter	No change
20	60	20	Colour very slight	Colour very slight	Colour very slight
20	40	40	" " "	" " "	" " "
20	20	60	" " "	" " "	" " "
20	0	80	Tinge of green	Tinge of green	Tinge of green
0	100	0	} White	} White	} White
0	80	20			
0	60	40			
0	40	60			
0	20	80			
0	0	100			

cobalt oxide direct, it may with advantage be previously mixed with finely-powdered flint or, preferably, with china clay, calcined, and the product ground to an impalpable powder. If a solution of a cobalt salt is used, care should be taken that it is not precipitated by any free alkali in the clay prior to the colour and clay being mixed, or it will form blue spots. When the solution of the cobalt has once been thoroughly distributed through the mass, it may, with advantage, be rendered insoluble by the addition of a solution of sodium carbonate.

Yellow goods (apart from those artificially coloured) may owe their colour to:

- The presence of only a small proportion of iron compounds, as in fireclays.
- The presence of finely-divided iron oxide simultaneously with free alumina.
- The presence of a considerable proportion of chalk or other form of calcium carbonate in clays burned in contact with coke or other organic matter.

Thus, true marls or malms are yellowish or whitish when fired, on account of the lime present in them, the London malms burning to a rich brimstone colour.

Buff-coloured Articles. The buff colour of bricks is due usually to the presence of iron compounds in some form, but the cause of the colour in buff-burning clays is far less clearly understood than that of either the red or white-burning clays. The iron content varies from 0.50 per cent to 4 or 5 per cent, with an average about 1.5. Buff-burning clays do not burn buff because of the exact amount of iron they contain. So far as the iron content is concerned, they might burn either red or white, and other conditions are far more important than the proportion of iron present. Sometimes the buff colour may be due to the effect of the iron compounds partly being reduced in the presence of lime compounds or free alumina, though this is not the case with fireclays, unless it is correct to assume that their buff colour, when burned, is due to a compound of iron and alumina.

Fireclays are usually buff colour when burned, but it has never been satisfactorily proved that this is due to the presence of iron compounds. The greater part of the iron in fireclays is in the form of pyrites or nodular ironstones which form black spots or blotches or patches of a dark-brown colour. Some fireclay articles have a reddish appearance (termed 'flashing', p. 828), due to the oxidation of iron compounds derived from the ash of the fuel used in firing. This usually occurs when an excessive supply of air is allowed to pass through the kiln during the cooling period.

The colour of fireclay articles must not be regarded as a criterion of their quality, as a dark-coloured brick, which, from its colour, might be rejected as too impure, may be more durable than a light-coloured one. Many engineers, architects, and builders consider that a fireclay article which has a good uniform buff colour is the best, their idea being that it has been burned at a high temperature without showing any signs of being affected by the heat. This is an entirely erroneous idea, for underburned firebricks are light coloured, and those which have been intensely heated are usually highly discoloured. In fact, a fireclay article of apparently poor quality, which is covered with blotches and much discoloured, may be better than one of a pleasant, pale-cream colour. In other words, discoloration is usually a sign of a high firing temperature, and when a firebrick has been heated to a temperature sufficient to produce blotches without the article itself being fused or warped, it is usually reasonable to suppose that it will be able to withstand that temperature when in use, whereas pale-coloured goods which have not been heated so strongly may fail in use.

Such deductions must not be carried too far. The advent of tunnel kiln firing of refractories in which the atmosphere surrounding the ware is maintained clean and oxidising has largely eliminated the brown, vitreous surface of fireclay bricks, which was caused by flame-flash or alkali impurities from coal ash used in burning the ware in Hoffman or intermittent kilns.

The presence of *minute* dark blotches of 'slag' in firebricks are of little consequence and are not detrimental to their quality, unless very abundant. Even then, if they occur chiefly at the surface, and are not abundant in the interior of the article, they will do little damage, though they create a very unpleasant appearance. Some users insist that the area of the dark spots in firebricks shall not exceed 3 per cent of the cross-section or face of a firebrick.

Clays which do not naturally produce a buff colour when burned may be made to do so by (i) destroying the colour of a red-burning clay by adding a large proportion of chalk or limestone; (ii) by adding iron in the form of a silicate mineral such as granite, schist, talc, etc., to a white-burning clay; (iii) by adding an iron solution to a clay slip and precipitating the iron by the addition of soda solution; and (iv) by adding a stain containing 95 per cent of alumina plus 5 per cent of oxide of iron, derived from ferric chloride solution by precipitation, as in (iii). This last gives the best results, but is costly, and to get the best effects the body must be heated to vitrification.

Brown goods are often produced by iron oxide in a clay, the conditions of firing being such that instead of the iron compounds attaining their full red as in red bricks, the colour is either partially developed or it is converted into a brown by overheating. The imperfect development of the red colour may be due to the presence of lime, alumina, and other substances in the clay, or to vitrification having set in before or after the red tint was fully developed.

The brown colour of some fired clays is due to the presence of manganese compounds.

ARTIFICIAL COLOURS

ARTIFICIAL colours¹ are produced by the use of various chemical substances which when heated to a suitable temperature assume the desired colour. The temperature to which the articles are heated must, therefore, be one which suits the colours. Thus, if the ware requires a high temperature for firing and the colour requires a low one, the ware must be burned first, then coloured and refired at a lower temperature. If, however, the colour will stand the temperature required to fire the ware, the latter may be first coloured and then fired. Where it is desired to mix a colour with the material of which an article is made, that colouring agent must necessarily be able to withstand the temperature at which the article is fired.

The finer colours and those produced by expensive chemicals are usually mixed with an engobe or glaze, and are then applied to the ware; to mix such colours with the whole of the clay of which the articles are made would not only be excessively costly, but would be an unnecessary waste of colour. Several firms supply colours prepared ready for use by potters and others.

Black articles or the nearest approach to a true black which can be obtained in pottery manufacture—may be produced by:

(a) The addition of a mixture of manganese dioxide and iron oxide to the clay or engobe. Where there is sufficient iron oxide in the clay, the addition of a suitable proportion of manganese dioxide is usually sufficient. The precise colour produced depends on the relative proportion and fineness of the two colouring agents. A red-burning clay with the addition of about $1\frac{1}{2}$ per cent of manganese dioxide will usually produce a beautiful jet black. It is important to use fine precipitated manganese dioxide; that produced from spent material used in the manufacture of chlorine, etc., is much less satisfactory. If the colour is too brown or violet, the proportion of manganese dioxide should be increased or the iron oxide reduced.

¹ The colouring agents used for glazes have been described in Chapter VI. (p. 354). Those listed here are used mainly as body colours for clay articles.

(b) The addition of a mixture of iron and cobalt oxides.

(c) The addition of iron, manganese, cobalt, and chromium oxides to the clay or engobe.

Grey may be produced by the use of smaller proportions of the same materials as are used for blacks (*supra*), but the iron must not be present in very large proportions when light shades of grey are required. Greys may also be produced by means of iridium oxide or platinum chloride or both, but these are so costly that their use is confined to the most expensive pieces of art ware.

Blue colours are produced in white wares by the addition of cobalt oxide to the clay or engobe. The shade of colour is largely dependent upon the alumina present, a highly-aluminous body giving a sky-blue tint, whilst a siliceous mass, or one containing zinc oxide, usually assumes more of an indigo shade. Blues may be modified by varying the proportion of cobalt and also by the addition of other substances, such as alum or frits.¹

Violet colours are extremely difficult to obtain; the best are usually produced by a mixture of chromium and cobalt oxides. Under suitable conditions, precipitated manganese dioxide produces an excellent violet.

Green colours are generally produced by the addition of chromium or nickel oxides to bodies containing only a very small proportion of iron oxide, as otherwise the colour will not be pure green. Chromium greens are the most easily produced, and may be modified towards blue by the addition of cobalt oxide. Nickel greens are somewhat uncertain, especially at temperatures above 1100° C., when no other ingredient is used, but with cobalt oxide a fairly reliable olive-green is obtained.

Copper oxide also produces a series of green colours, but they are more easily spoiled at high temperatures than chromium greens.

At temperatures above 1200° C., iron silicates impart a greenish-yellow colour to the ware, whilst when such silicates fuse they become quite green and produce the colour of green bottles.

Yellow colours are, where possible, produced almost entirely by iron oxide, the tints varying from yellow through orange to yellowish brown. For high-class pottery, titanium and antimony oxides or lead chromate may be used. For orange-yellow tints, uranium oxides may be employed. For these tints an oxidising atmosphere is essential, as a reducing atmosphere gives a greenish-grey shade.

Red colours, produced at comparatively low temperatures, are usually due to iron oxide. In vitrified wares, iron oxide seldom produces a pleasing red shade. A rose or pink colour may be produced by the addition of a finely powdered frit of bichromate of potash and alumina, whilst a lilac tint may be obtained by the addition of a little cobalt oxide.

Occasionally bricks are made to appear red by dipping them in, or painting them with (just prior to sale), a slip prepared by mixing Venetian red with water into a pulp, which is pressed through a sieve to break up lumps that are formed in mixing,

¹ A *frit* or *fritt* is a partially fused mixture of two or more substances, some or all of which could not be used separately on account of their solubility in water. In the process of fritting, chemical combination occurs and insoluble substances are produced. The process of fritting is also used to distribute a small proportion of a strong colouring agent in a large proportion of white or colourless material, so as to produce a lighter tint than would otherwise be possible.

and then adding enough stale ale or beer to make the stain of a proper consistency. To each gallon of this mixture is added one quarter of a pound of calcined iron sulphate, previously beaten up with a portion of the stain to a thin batter. This is the mordant or fixture, without which the stain would finally wash off from the effects of the rain.

A more durable and permanent stain is made with Venetian red that has been ground with linseed oil to form a stiff paste, or, if the stain is to be of a lighter shade, a mixture of Venetian red and French yellow ochre, both ground fine in linseed oil and beaten up with a small portion of a good turpentine japan to a smooth semi-paste, gradually adding in small quantities while stirring, a mixture of one part (by measure) of 90 degrees benzol or good solvent coal-tar naphtha and four parts (by measure) of turpentine, until the proper consistency of stain is secured. The liquid is strained through cheese-cloth and the coarser particles thrown away, as these would remain on the surface and be of no benefit in sealing the pores of the brick. An excess of oil in the stain is apt to produce 'shiners', but has the additional advantage of rendering the bricks waterproof. These pastes are paints rather than ceramic colours.

Brown colours are obtained with iron oxide at a temperature higher than that necessary to produce a good red. This treatment is usually accompanied by a variable amount of vitrification. For the lower temperatures a good brown shade may be obtained by the addition of a little manganese dioxide to a ferruginous body. Thus, the addition of 0.5 per cent of fine manganese dioxide will produce a beautiful chocolate tint.

Browns may also be obtained by (a) mixtures of iron and chromium oxides, (b) iron chromate, (c) manganese and chromium oxides, (d) a frit composed of zinc sulphate and chromium oxide.

To secure the desired colour when special colouring agents are employed, it is most important that the right atmosphere should be maintained during the firing of the ware and that the right temperature should be reached, but not exceeded. Excessively high temperatures may cause volatilisation of the colour. Very often in producing coloured goods, different effects are obtained on account of variations in the state of the atmosphere in the kiln. Thus, articles intended to be buff may be streaked with red, red ones may be changed to chocolate colour or purplish black, whilst blue ones may be considerably deepened. These accidental shades of colour are often of great beauty, but cannot always be produced as and when desired.

The effect of the atmosphere in the kiln upon various colours is shown in Table XIV.IV, due to Le Chatelier and Chapney.

The volatilisation of some colours also produces a vari-coloured effect (often of great beauty). Volatile chlorides are largely used for the production of this class of ware, lead chloride being commonly employed. By the use of a chlorinated atmosphere, such as is produced by this means, cobalt oxide will give a blue colour, nickel oxide a brown one, copper oxide green at low temperatures, and iron oxide a very unpleasant yellow. The production of colour effects by partial volatilisation is known as 'flowing'.

Streaks of colour are often useful as a form of decoration. They are sometimes caused by firing a glaze to such an extent that it vitrifies and flows; by this means very beautiful marbled effects may be obtained.

Variegated colour effects may also be obtained by the process known as 'flaming' or 'flashing'.

A surface coloration of common and facing bricks is being employed on an increasing scale. Extruded shapes are more easily treated although the technique has also been adapted to bricks moulded by machine. The colour to be applied is usually mixed with sand or clay and sprayed or rolled on to one or more surfaces of the shape. Many pleasing effects can be produced in this way and clays with an unsatisfactory colour can be utilised. In addition to colour, designs or patterns can be imprinted on the surface of extruded bricks by simply-contrived appliances. These may produce no more than regular striations or furrows, but the overall effect on a large area of brickwork is highly satisfactory.

TABLE XIV—IV. EFFECT OF HEAT ON COLOURS

<i>Compound of Metal in Colour</i>	<i>Firing Cone</i>	<i>Temperature °C.</i>	<i>Colour produced in Oxidising Atmosphere</i>	<i>Colour produced in Reducing Atmosphere</i>
Chromium	13	1380	Violet, blue, green, gold, orange, or red	—
Cobalt			—	Blue, green, or rose
Copper			Blue, green, gold, or red	Blue, green
Iron			Gold, red	—
Manganese			Violet, blue, green, gold, red	—
Nickel			Violet, blue, green, gold, red	—
Titanium			—	Violet, blue, green, gold, red

THE COLOURS OF CERAMIC MATERIALS OTHER THAN CLAY

THE colour of ceramic materials other than clay is not often of great importance except as a very rough indication of their quality, though it should be remembered that the remarks on p. 824 with reference to the relation between the colour and properties of fireclay bricks apply to most other ceramic articles.

Siliceous Materials. Pure *quartz* is colourless, but natural quartz is often rendered partially opaque by numerous 'inclusions' or bubbles, and it is frequently tinted by an iron oxide and other impurities which impart to it a pink, yellow, brown, or purple colour; sometimes it is so dark as to appear almost black.

Quartzites, if quite pure, would be colourless, but they are invariably tinted by traces of iron and other oxides and so vary from white to a dark brown, the purer and more refractory qualities being almost colourless. Many quartzites which appear to be opaque or coloured, consist of transparent, colourless grains, the opacity, and to some extent the colour, being a mass-phenomenon.

Ganister varies from grey to dark brown in colour according to the proportion of carbonaceous matter, iron oxide, and clay present. The individual grains are transparent and usually colourless.

Flint varies in colour from grey to almost black, apparently on account of the extremely fine state of subdivision in the material and the large amount of consequent internal reflection.

Chert is similar, but much lighter in colour, as also are *chalcedony* and other forms of amorphous silica. *Chalcedony* is generally white, grey, pale blue, bluish white, or brown in colour.

Kieselguhr varies greatly in colour according to its purity. The best qualities are white and are composed of colourless grains, but inferior deposits are often coloured deep red or brown by ferric oxide. In some deposits of *kieselguhr* the red colour of the iron oxide is masked in the raw state by carbonaceous matter, which imparts a greyish tint to the material. On calcination, the carbonaceous material burns away and the red colour is restored. The *kieselguhr* at Naterleuss, in Germany, is coloured green by the presence of a large proportion of carbonaceous matter.

When heated to bright redness in an oxidising atmosphere, quartzite, ganister, and other siliceous materials are usually white, the less pure ones being pale yellow or buff and often contain dark-brown spots of iron compounds.

Carbon. *Graphite* is greyish black with a metallic lustre. *Coke* has a steel-grey tint. Their colour is not appreciably altered by heat, but in the presence of air they are gradually converted into a colourless gas.

Silicon carbide varies in colour according to its form. The crystals vary from pale yellow to grey or blue-black, and the amorphous variety, known as *firesand*, is white when pure, but the commercial material is usually green, grey, or nearly black with a bluish sheen. The colour is not affected by heating to redness.

Bauxite, when pure, is white, but as some iron compounds are generally present its colour is sometimes pale grey, yellow, or even brick-red. The much rarer blue bauxite appears to owe its colour to colloidal ferrous sulphide.

When heated to bright redness in an oxidising atmosphere, bauxite varies from nearly white to a reddish or brown tint according to the iron oxide present.

Crystalline magnesite is colourless, white, or yellowish grey. The cryptocrystalline magnesite is white, yellowish, or brown. *Hydromagnesite* is usually white and resembles chalk. *Breunnerite* is generally grey or yellow when freshly cut, but on exposure the iron compounds present are oxidised and impart a brownish colour to the rock.

When heated to bright redness, pure magnesite remains white, but much of the natural mineral is coloured buff or reddish brown by the iron oxide and other impurities present.

When most samples of pure magnesite are heated to 1500° C. or above (i.e. when they are dead-burned), they remain white, but in most commercial samples of natural magnesite the effects of the colouring agents are accentuated and the product is buff, red, reddish brown, chocolate brown, or black, according to the nature and proportion of impurities present. When different samples from the same deposit are compared, their colour is a useful indication of the extent to which the magnesite has been heated, though the change in colour is much less marked with the purer magnesites. Thus, a properly dead-burned and sintered magnesite containing about 4 per cent of iron oxide is a dark chocolate-brown colour, but if the same rock has not been heated so intensely it is much lighter. The darkest colours are usually due to a partial reduction of the iron oxide or to the presence of manganese compounds. The difference in colour between pure and slightly ferruginous magnesite is clearly

shown in magnesite bricks. Those made from magnesite which contains ferric oxide, are reddish to dark brown or black, whilst those made from the much purer Grecian magnesite are cream, buff, or other light colour, and frequently have numerous dark-brown spots.

Dolomite varies in colour from pale cream to yellowish brown according to the amount of iron oxide present. The colour of calcined dolomite and of any bricks, etc., made from it, is usually yellowish brown.

Lime, when almost pure, is perfectly white, but portions of commercial limes are usually coloured slightly by iron oxide or charred carbonaceous matter. Refractory bricks and blocks made of lime should be almost pure white.

Zirconia. The natural mixture of zirconia and zircon found at São Paulo, Brazil, varies from grey to bluish black, according to its purity. It is a curious fact that the ore richest in zirconia is almost jet black, because pure zirconia is a brilliant white. The baddeleyite found in Ceylon varies in colour from white to grey-brown, bluish black, or dark green. Natural zircon is usually tinted yellow by the iron oxide present, and some specimens are grey-green or red. The colour of pure zirconia when calcined is white if the temperature has not exceeded 1500° C., but above this temperature various colours are developed as a result, according to Ruff and Lauschke, of the formation of nitrides, lower oxides, and black zirconium carbide.

When titanium oxide is present in zirconia, a bluish colour is developed at a temperature of about 1500° C.

DISCOLORATION

THE term 'discoloration' is applied to materials or articles possessing colours of an undesirable nature upon their surface or in their interior. Such a defect is due, in the main, to the same causes as the colours previously mentioned. The principal causes of discoloration are:

- (a) Insoluble substances.
- (b) Soluble substances or 'scum'.
- (c) Substances derived from the fuel and present in the kiln gases.
- (d) Substances volatilised from articles adjacent to the ones which are discoloured.

Discoloration by insoluble substances includes several colouring agents mentioned in preceding pages which produce an undesirable appearance.

Black spots are usually due to ferrous or manganese compounds, but sometimes white ware fired in silicon carbide saggars is discoloured by grey, red, or black stains, due, according¹ to H. Spurrier,¹ to the production of volatile ferro-carbonyl compounds.

Blue discolorations in china are often due to ferrous phosphate (derived from bone ash containing carbon), a deficiency of alkalis in the body, or to the action of reducing gases.

Brown discolorations are usually due to ferric compounds including absorbed vapour of ferric chloride and also the discolorations in china due to ferric phosphate.

¹ *J. Amer. Ceram. Soc.*, 4, 923, 1921.

Some pieces of white china become discoloured with brown patches on prolonged exposure to air; these discolorations are also attributed to ferric phosphate. For information on brown discolorations of firebricks, see p. 824.

Ferrous phosphate is sometimes white, but on exposure to air it becomes blue or green, and finally develops a brownish crust by oxidation. See also *Brown scum*, p. 832.

Green discolorations may be produced by copper and vanadium compounds; thus, cupriferous pyrites produces greenish slag spots and vanadium molybdate produces irregular green patches.

Green discolorations may be due to the slight deposition of soot on the goods or to the causes of black discolorations operating on a smaller scale.

Pink discolorations on biscuit ware or buff terra-cotta often indicates that the ware has been heated too rapidly below 700° C., so that the combined water has not been driven off properly. This fault is known as *steaming*.

The red discoloration in some hard porcelain, known as *la malade jaune* or *jaune de cuisson*, is due, according to B. Moore and J. W. Mellor,¹ to the presence of ferric oxide and of oxidising conditions in the first stages of burning. Seger found that a red discoloration which occurs on a yellow-burning clay may usually be cured by alternately heating in a very smoky kiln (i.e. in a strongly reducing atmosphere) for some time and then in an oxidising atmosphere, at intervals of eight hours, so as to cause the sulphur to be evolved as sulphuric acid and to reduce the iron to a ferrous state.

Yellow discolorations are often due to ferric compounds. For means of correcting a yellowish tinge in china and white earthenware, see p. 822.

Scum is a defect known by a variety of names, such as *whitewash*, *nitre*, *salt*, *mould* (all of which are incorrect), and *florescence*, *efflorescence*, *wall-white*, *kiln-white*, etc., which more accurately describe it.

In recent years it has become customary both in Great Britain and the United States to reserve the term *scum* for substances actually formed or deposited during processing as in the dryers or kilns, and *efflorescence* for effects caused by materials originally present in the clay or formed during firing which show up only after periods of exposure to the weather.

Scum. The chalky-white or vari-coloured film or deposit which is occasionally observed on ware at some stage of the processing is referred to as scum. It has been attributed to either:

(a) Soluble salts present in the clay being transported to the surface of the ware during the removal of water. These are chiefly calcium, magnesium, potassium, sodium, ferrous or aluminium sulphates and occasionally chlorides and nitrates. Such salts are of more frequent occurrence in weathered clays or rocks than in those which have been freshly dug or quarried.

(b) Substances deposited on or formed on the surface during the drying or burning, either by condensation products from the hot gases or by some chemical reaction taking place within the kiln. Sulphurous fumes are the most objectionable because these readily form sulphates in the presence of moisture.

¹ *Trans. Eng. Ceram. Soc.*, 16, 58, 1917.

(c) The migration to the surface due to incorrect drying practice of fine-particled material contained in the clay. The surface layers of bricks dried on hot floors are frequently enriched in clay in this way but this may not cause a serious deterioration in fired colours; finely-divided calcium carbonate, usually present as chalk may also be concentrated and in such clays the fired colour is always affected. Fine silica sand in a clay can also cause troublesome effects.

White scums are the commonest and include 'kiln white' and 'dryer white'. The former consists chiefly of calcium sulphate with small amounts of magnesium and alkaline sulphates, and occasionally a trace of alum. It is more usually attributable to the action of sulphurous fumes in the kiln gases which act on the lime, etc., in the clay.

A *brown scum* on some fired goods may be due to the presence of soluble iron salts formed by the oxidation of pyrites in the clay or rock to ferric sulphate which, being soluble, rises to the surface of the moist material by capillary action during the drying and is converted to ferric oxide during the firing.

A *grey scum* is sometimes formed if calcareous water comes into contact with a clay. Calcium and magnesium sulphates, when present in a clay, also tend to impart a drab appearance.

A *yellowish scum* may be formed by the interaction of sulphuric acid in the kiln gases with alumina, lime, and silica in the clay at temperatures approaching that of vitrification. Seger found a yellowish-green scum to be produced by the presence of soluble vanadium and molybdenum compounds.

The prevention of scum is best effected by drying the articles correctly and thoroughly in an atmosphere free from sulphurous fumes. During the initial firing the sulphur content of the gases should also be kept to a minimum in order to reduce 'kiln white'. 'Dryer white' can be reduced only by careful humidity drying or by reducing the content of soluble salts in the raw clay (see also under efflorescence).

Scum is undesirable in that it leads to an unsightly appearance of the ware. The localised concentrations of such salts as calcium and magnesium in the surface layers of the body may seriously affect the colour on firing and so destroy the required red shade of many facing bricks.

Efflorescence. Some bricks are apparently perfect in colour after firing, but when exposed to the weather for a period of time, an unpleasant film or scurf forms which is usually white or grey with a characteristic crystalline appearance. This is efflorescence and it is due to a variety of causes:

- (a) Soluble salts occurring naturally in the clay itself.
- (b) Soluble salts produced from other ingredients in the material as a result of weathering.
- (c) Soluble salts produced by interaction between the component minerals in the clay during firing, or by the action of furnace gases on some component within the clay.
- (d) Soluble salts contained in the mortar used in erecting a building of the bricks.
- (e) Soluble salts developed by interaction of the mortar and bricks or tiles.

(f) Soluble salts in the water used in the manufacture of the ware, or which later gains access to the structure.

(g) Soluble salts in the ground on which the goods are stacked, or in ashes or other materials which come into contact with the ware.

Similar colorations may appear as in scumming and the same salts may cause both these defects, though the formation of each is rather different. In a brick which exhibits efflorescence, the soluble salts are initially uniformly distributed throughout the body. Successive impregnations and dryings when exposed to the weather, result in the soluble components being brought to the surface by capillary action. Many salts, for example, calcium and magnesium sulphate, absorb water from the atmosphere and form a hydrate, and in the process undergo a large volume expansion. When this occurs within the surface of the brick, especially if the porosity is low, crumbling and disruption may result. Calcium sulphate, in amounts as low as 0.1 per cent may cause serious efflorescence, but magnesium sulphate is even more deleterious and 0.01 per cent of this component may produce undesirable results.

Soluble sulphates are not of frequent occurrence in raw clays. They are liable to form, however, when pyrites and carbonates are present together and when the firing is not wholly under oxidising conditions. Sulphurous gases in the kiln may also react on the carbonates and other minerals to form the corresponding sulphates.

Efflorescence may be prevented or reduced in the following ways:

1. By adding barium carbonate or chloride to the clay; this converts any soluble sulphates into insoluble barium sulphate and renders them harmless. This treatment is not effective for other salts which cause efflorescence.

2. By maintaining oxidising conditions during the initial stages of burning and reducing the sulphur content of the kiln gases to a minimum.

3. By avoiding the use of water or mortar containing soluble salts.

4. By avoiding contamination of the material at all stages of manufacture.

5. By painting the surface of brickwork with a solution of a silicone or other organic silicate compound. Although this is an expensive method it is most effective.

The *efflorescence tendency* of a brick can be measured by the Wick test or a modification of it.¹ A whole brick is set on end in a bath of distilled water to a depth of 1 in. and left for seven days. The level of water must be maintained constant throughout this time. Water is taken up in the pores of the brick, dissolves any soluble salts and transports them through the brick to the upper parts where surface evaporation occurs. After seven days, the brick is thoroughly dried in an oven and afterwards examined for discoloration effects. The American Society for Testing Materials specifies that at least five bricks should be tested, but on no account must bricks of more than one type be placed in the same pan of water otherwise contamination of one by others may occur.

Mottling in silica bricks is a form of scumming where acid fumes in the kiln gases react with iron-bearing minerals in the moulded brick. This occurs only in certain regions so that the surface has a characteristic mottled appearance with large patches of red coloration on a yellow or buff background. These stains are restricted to the surface layers and do not influence the properties of the brick in any way.

¹ A.S.T.M. Brick Specification C67-50; *British Standards*, No. 1257, p. 8, 1945.

Mottled surfaces on glazed wares are due to a variety of causes, including defective protection when placing in the oven or kiln, imperfect mixing of the ingredients in the preparation of the body, engobe or glaze, and the shape of an article which causes a coloured glaze to flow irregularly. After firing in the kiln, bricks which normally burn to a light colour, sometimes have a surface discoloration which may be red or brown. This effect may be confined to one or two bricks or to parts of bricks, but in some cases a complete setting may be influenced. This is known as *steaming* and the discoloration is usually characteristically streaked, so that it is often mistaken for 'flame-flash'.

Steaming is caused by (a) the ware being set in a wet condition and heated too rapidly in the initial stages of kiln firing, or (b) warm, humid gases circulating round the ware during firing and water condensing on the cold articles. Although it has not been definitely established, it is most likely that sulphurous fumes in the kiln gases combine with iron compounds in the clay when water is present, render them soluble and then they are drawn to the surface during drying out.

The discoloration effects of steaming spoil the appearance of the ware, but it is indicative of a serious condition in the kiln. When the amount of water, present in the kiln in the early stages of firing, becomes excessive, the bricks are liable to become fused together or to crack. In serious cases, the complete setting in a kiln may slump or collapse.

HARDNESS

THE term 'hardness' cannot be applied to ceramic materials with exactness as there is no satisfactory definition of it. Hardness is commonly understood to mean resistance to scratching but it is often used to imply resistance to *abrasion*.

A comparison of the hardness of clays and many refractory materials, both in the raw and fired states, is often a matter of great difficulty, because these materials are not strictly homogeneous and different portions of them have different degrees of hardness, so that no single figure can accurately represent the hardness of the material. For instance, the outside 'skin' of a brick or tile is usually much harder than its interior; many firebricks are composed of mixtures of burned clay and quartz, which substances differ greatly in hardness, and in many articles, the bulk of the material or aggregate has a hardness which is different from that of the bonding material. When the hardness of a heterogeneous substance is considered, the term usually relates to that of the material as a whole and is, therefore, only capable of a relatively rough measurement.

Hardness is usually measured by observing the resistance of the materials to (a) indentation, and (b) abrasion by various harder substances. There is no direct relation between the resistance of a heterogeneous substance to indentation and to abrasion, as the latter is not really a measure of the hardness of the material as a whole, but of the bond, for no matter how hard the individual grains of aggregate may be, if the bond is soft and easily abraded the whole material will rapidly be worn away. Hence, the hardness of a heterogeneous substance is closely connected with the cohesion of the various particles.

Resistance to indentation may be measured by a scleroscope or by a Brinell ball, but for rough-and-ready comparisons a 'scratching test' is chiefly used. A series of

minerals of different hardness is used, and each of these is drawn across the material to be tested so as to make a scratch if the latter is softer than the former. When the material to be tested is scratched by one member of the series, but scratches the next softer member, it is said to have a hardness between that of the two members. The series of minerals generally used for the purpose is shown in Table XIV.V, where they are arranged in what is known as 'Mohs' scale'. A series of convenient substitutes is also shown in the same Table.

A scratching test is, at best, only a rough one, but it is extensively used because of its convenience. No really satisfactory means of determining the hardness of ceramic articles has yet been devised.

When a substance has a crystalline structure its hardness will vary along different planes and is usually lower in the direction of cleavage than perpendicular to it.

TABLE XIV—V. MOHS' SCALE
(substitutes shown in *Italics*)

<i>Hardness No.</i>	<i>Material</i>
1	Foliated talc
2	Rock salt or gypsum, or <i>finger nail</i>
3	Transparent calc spar or <i>copper wire</i>
4	Fluorspar, <i>scratches copper wire</i>
4-5	<i>Ductile iron; window glass</i>
5	Transparent apatite
5-6	<i>Blade of good pocket-knife</i>
6	Orthoclase felspar
6-5	<i>File</i>
7	Transparent quartz
7-8	<i>Will scratch a knife</i>
8	Transparent topaz
9	Sapphire or corundum
10	Diamond

HARDNESS OF RAW MATERIALS

THE hardness of raw **clays** varies greatly, from less than 1 to more than 7 on Mohs' scale; some surface clays are quite soft and can be cut with a knife; others, such as shales and rock clays, are hard, because of the metamorphic changes they have undergone and the pressure to which they have been subjected. *Marls* and *fireclays* vary greatly in hardness, according to their mode of formation and location; most of them, when in the dry state, can be easily cut with a knife, but some are hard enough to scratch glass. This scratching is largely confined to siliceous (quartzose) impurities in the clay and not to the clay itself. Ayrshire bauxitic clay and some American flint clays are extremely hard due to their mode of origin and subsequent alteration.

As clays are usually converted into a plastic paste, or into a slip or cream before use, their hardness is chiefly of importance in so far as it affects the methods to be employed in grinding them to powder or otherwise preparing them for use. Clays which can readily be crushed to the required fineness are naturally easier and cheaper to prepare and are, therefore, more desirable than very hard materials which require much power to reduce them.

A property similar to the Brinell hardness of raw clay is the 'pressure of fluidity'. A. S. E. Ackermann¹ found that if a horizontal disc of metal is placed on plastic clay and loaded, each increment of load causes an increase in the penetration up to a certain critical point, at which the disc continues to sink at about ten times the previous rate without any increase of the load. This critical point is termed the pressure of fluidity and varies according to the amount of water in the clay and, therefore, to the plasticity; it is discussed in Chapter VIII in connection with the mobility of clay pastes.

TABLE XIV—VI. HARDNESS OF CERAMIC MATERIALS
ON MOHS' SCALE

<i>Material</i>	<i>Hardness</i>	<i>Material</i>	<i>Hardness</i>
Agate	7	Kaolinite	1-2.5
Apatite	5	Kyanite	7
Baddeleyite	6.5	Magnesite	3-5
Bauxite	1-3	Magnetite	5.5-6.5
Boron carbide	9-10	Mica	3
Brookite	5.5-6	Monazite	5-5.5
Calcite	3	Periclase	6
Chromite	5.5	Quartz	7
Coal	2.3	Rutile	6-6.5
Common clay (dry)	0-4	Sand	7
Corundum	9	Silicon carbide	9-9.5
Dolomite	3.5-4	Sillimanite	6-7
Felspar (orthoclase)	6	Spinel	7-8.5
Fluorspar	4	Talc	1
Graphite	1-2	Tantalite	6
Gypsum	2	Titanite	5-5.5
Haematite	5.5-6.5	Tridymite	7
Hydromagnesite	3-5	Zircon	7.5
Ilmenite	5-6		

Silica has a hardness of 7 on Mohs' scale, but many siliceous materials in which individual grains are very hard may be easily crushed, as the bond which unites these particles is quite weak. For the same reason, the individual grains of silica in articles made of that material are much harder than the average hardness of the articles, on account of the softness of the bond.

Aluminous materials vary greatly in hardness; bauxite usually has a hardness of 1-3 on Mohs' scale, whilst corundum has a hardness of 9-10 and is one of the hardest substances known.

Magnesite varies in hardness according to the form in which it occurs. Coarse crystalline magnesite usually has a hardness of about 4 on Mohs' scale, whilst crypto-crystalline magnesite has a hardness of 3-5 and hydromagnesite a hardness of 3-5.

Carbides, nitrides and carboxides are extremely hard, corresponding to 9-10 on Mohs' scale, being harder than crystalline alumina (9), but not so hard as diamond (10). The hardness of various minerals which are used in the ceramic industries is shown in Table XIV.VI.

¹ *Trans. Society of Engineers*, 1910.

Sintered Oxides and similar materials can be very hard, so much so that they have been used to replace the more expensive carbide tools in steel-turning and for other applications.

HARDNESS OF BURNED CERAMIC MATERIALS

Burned clay is much harder than raw clay and articles composed of it, either alone or mixed with other materials, may conveniently be arranged¹ in two groups, according to their hardness:

Group I.—Soft wares, which can be scratched by iron, including fired sandy-clayed bodies, such as bricks, cooking utensils, crucibles, jars, unglazed earthenware, faience, roofing tiles, and most refractory materials.

Group II.—Hardwares, which cannot easily be scratched by steel, including fine earthenware, ceramic stoneware, pipeclay ware, flint ware, and hard china.

The resistance of ceramic materials to abrasion is usually more important, especially as many of them are subjected to a considerable amount of abrasion when in use. Thus, domestic pottery requires to resist the scratching and rubbing action of knives, forks, etc.; paving bricks, floor tiles, etc., require to be resistant to traffic; and many refractory materials are required to resist the abrasive and corrosive dust contained in the hot gases in furnaces, kilns, etc., which rapidly wear away any soft portions of refractory material.

The bricks which form the lining of vertical shaft furnaces, such as blast furnaces, cupolas, lime, magnesia, and other calcining kilns, etc., are subject to great abrasion by the descending charges, and it is essential that such bricks should have the necessary resistance to this action and to the differential movements which often occur in shaft kilns and also exercise a considerable abrasive action.

The manner in which gas retorts and some other appliances made of ceramic materials are charged and discharged also calls for the use of a material which is highly resistant to abrasion both in the hot and cold states. 'Rough usage' also has a great abrasive effect, as well as necessitating the use of a material which is resistant to blows and shocks.

The resistance of a ceramic material to abrasion depends upon one or more of the following:

- (a) The nature of the material, and especially its texture and hardness.
- (b) The mode of its preparation.
- (c) The nature of the bond (if any).
- (d) The amount of bond (if any).
- (e) The extent of vitrification.
- (f) The temperature of the material when it is examined.

Building Bricks. The hardness of building bricks is seldom of much importance, as, in the ordinary way, they are not required to be highly resistant to abrasion. Most well-burned bricks are rather harder than sandstone. Very soft bricks should not be used, except, possibly, as panels in interior work, as they are generally underburned and deficient in strength and resistance to the weather.

¹ Brongniart, *Treatise on the Ceramic Arts*.

Bricks are not of strictly uniform hardness throughout their mass and the surface is usually harder than the interior on account of the greater pressure applied to it.

The Brinell hardness of various bricks, compared with metals, is shown in Table XIV.VII, due to H. Le Chatelier and B. Bogitch.¹

TABLE XIV—VII. BRINELL HARDNESS
OF VARIOUS MATERIALS

<i>Material</i>	<i>Diameter of Depression</i>
Copper	4.5
Lead	10.1
Hard face brick	4.5-8.8
Soft face brick	6.8-12.0
Fireclay brick	6.0-6.2
Hard silica brick	5.0-5.1
Tender silica brick	10.1-10.7

There appears to be no definite correlation between the hardness and the compressive strength of bricks and similar articles.

Vitrified bricks, when used for roads, etc., require to be specially resistant to abrasion, and, such bricks should not lose more than 14 per cent of their weight when subjected to the Standard Rattler Test, and no one brick should lose more than 18 per cent of its weight. The 'Rattler Test' is described in Chapter XIII.

Roofing tiles should be sufficiently hard to be handled without chipping and to prevent them from being damaged by frost. They should not be vitreous or they will 'sweat' when in use. A good roofing tile should usually be difficult to scratch with a piece of steel; roofing tiles which are harder than steel are generally too hard and vitreous. The desired hardness is largely determined by the manner in which the tiles are fired in the kiln. The temperature usually needed to secure roofing tiles of satisfactory hardness is between Cones 04 and 1a (1020° and 1100° C.).

Floor tiles should be sufficiently hard to resist any abrasion to which they may be subjected.

Fireclay bricks vary greatly in hardness, some being sufficiently soft to crumble when cut with a steel blade, whilst others are harder than steel. The hardness depends to a large extent upon the temperature at which the bricks are fired; the higher the finishing temperature the harder will be the bricks, and soft bricks are usually underburned.

The hardness of fireclay bricks by the Brinell method is shown in Table XIV.VII. The resistance to abrasion of various bricks, tested by M. L. Hartmann and J. E. Kobler, is shown in Table XIV.VIII, the method of testing being described on p. 841.

Nesbitt and Bell, who used a similar method for determining the resistance to abrasion, found that hand-made fireclay bricks were less resistant than machine-made ones, hand-made bricks being cut by abrasion to a depth of 0.04 in. in five minutes, whilst machine-made bricks, made by subjecting clay containing 7 per

¹ *La Céramique*, 371, 17-18, 1919.

cent of moisture to a pressure of 1500 lb. per sq. in., were cut to a depth of only 0.02 in.

Fireclay bricks when heated to a temperature below the melting point are more resistant to abrasion than when they are cold, but when at or above the sintering temperature the presence of molten material in them reduces their hardness and renders them much less resistant to pressure and abrasion. Sometimes, when bricks are taken out of a kiln, they appear to have softened greatly and become seriously distorted; this is not always the result of exposure to a high temperature, but is sometimes caused by condensed steam softening the freshly-set bricks some hours before their temperature has been raised appreciably above that of the atmosphere.

TABLE XIV—VIII. RESISTANCE OF REFRACTORY BRICKS TO ABRASION

<i>Kind of Brick</i>		<i>Depth of Cut when Cold</i>
		Inch
Silicon carbide brick	}	0.1-0.2
Zirconia brick		
Bauxite brick		
Grade C fireclay		
Magnesia brick	}	0.05-0.07
Chrome brick		
Silica brick		
Grade A fireclay	}	0.17
Grade B fireclay		
		0.25-0.26

Silica bricks are composed of hard grains, but the bond is soft, so that the bricks are readily rubbed down, and they resist abrasion only to a small extent. The hardness of the individual grains is equal to that of quartz (p. 836). The greater the proportion of lime used in making the bricks the harder will they be, as their resistance to abrasion is entirely dependent on the bond formed by the combination of lime and silica, and unless a sufficient amount of this bond is produced the particles of quartz, etc., are only feebly held together.

Silica bricks which have not been burned at a sufficiently high temperature are very soft and easily abraded. Well-burned bricks are harder and emit a good 'ring' when struck.

Fused silica is not so hard as some forms of glass, though harder than others. Its hardness is 5 (Mohs' Scale).

Magnesite bricks are fairly resistant to abrasion at atmospheric temperatures, but they are very soft at high temperatures.

Fused magnesia has a hardness of 5-6 according to Mohs' scale.

Bauxite bricks vary in hardness according to the material of which they are made. Their hardness is increased if the bauxite contains a moderate percentage of iron oxide, as, when heated to high temperatures, such bauxites produce a material corresponding to emery, and of such intense hardness that it can scarcely be cut by steel tools. At high temperatures they appear to be very resistant to abrasion.

Silicon carbide bricks are extremely hard, and an angular fragment from them will readily cut glass. At high temperatures some silicon carbide bricks appear to be extremely resistant to abrasion, more so than any other form of refractory brick.

Zirconia bricks vary in hardness according to the bond used. Zirconia itself is soft and remains so, according to H. C. Mayer, even when it has been heated to above 1427° C. The same authority has stated that a brick made of wet-ground material, containing 84 per cent of zirconia, was flint hard; the nature of the bond was not stated. According to R. C. Gosrow, zirconia bonded with magnesium chloride and fired at 1600° C. is extremely hard and scratches glass. This mixture retains its hardness when heated to a still higher temperature, zirconium carbide being sometimes formed.

Chrome bricks are fairly resistant to abrasion in the cold, but at high temperatures they are rather soft.

Glazed ware should be sufficiently hard to resist the abrasion to which it is subjected in ordinary use. Domestic earthenware is scarcely hard enough for severe use, as it is too easily scratched by knives and forks. Bone china is much better in this respect, and the 'hard porcelain' of the Continent is the hardest and most resistant of all such ware.

ABRASION

FOR many ceramic articles, resistance to abrasion is of minor importance, but in grinding-wheels and some cutting-tools a high abrading power is of great value. These articles are made of particles (of selected sizes) of diamonds, emery, silicon carbide, quartz (sand), glass and various synthetic materials such as fused alumina. The particles (known technically as *grit*) are mixed with a suitable bond such as rubber shellac, magnesium oxychloride, sodium silicate, a vitreous bond similar in composition to hard porcelain, or various resinoid materials such as bakelite. The articles are moulded from a stiff plastic paste, dried and baked or fired at a temperature corresponding to the nature of the bond and the hardness or grinding power desired.

An abrasive material must not only be hard—7–10 on Mohs' scale; it must also be tough and strong so that when the particles break they do so sharply and leave angular fragments behind to provide fresh cutting edges. (The effectiveness of most abrasives depends also on the pressure with which they are applied, the speed at which the abraded material is removed and, in the case of some metals, efficient cooling at the point of abrasion.)

For further information see 'Hardness' (p. 835).

Resistance to Abrasion is an important property of some ceramic materials; well-known instances are paving bricks, balls used in ball grinding mills, linings for grinding cylinders and the resistance of furnace linings to the downward movement of the charge. In all these instances, *toughness* rather than hardness is the most important factor. A finer texture is also desirable so that relatively large pieces are not torn out of their surroundings.

Resistance to abrasion can only be ascertained by full-scale trials as it is not proportional to the hardness scale nor has it any simple relation to any other property, though vaguely related to several such as the strength of the bond uniting the grains

together, and the modulus of rupture. There appears to be no co-relation between 'Hardness' ('scratch tests'), porosity tests and resistance to abrasion and very little between a sand-blast test of a brick proposed for use as a part of a furnace lining and the efficiency with which such a brick will resist abrasion when in use.

The resistance of plates and saucers to the abrasion of knives and forks is very important, as such ware when scratched is unattractive.

DETERMINATION OF HARDNESS

METHODS of determining hardness may be divided into three groups: (a) those in which the hardness is measured by the amount of material removed from a sample by abrading or grinding it with some other substance—the so-called 'abrasive tests', and (b) those in which the material to be tested is scratched by another material, e.g. a knife-blade or file, and (c) those in which the material is indented by pressure from a ball, cone, or edge-tool, to an extent which is assumed to be proportional to their hardness.

Abrasive tests are of two kinds: (i) those in which the sample is pressed against the abrasive material, and (ii) those in which the abrasive is projected on to the sample to be tested.

Bauschinger's abrasion-testing machine consists of a horizontal cast-iron plate or disc, 2 ft. 6 in. diameter, revolving at 30 revs. per minute. The sample, for instance half a brick, is weighed and is then pressed on to the disc with a pressure of 75 lb. The disc is charged with 20 grams of emery powder and revolved 22 times. The disc is then recharged with the same weight of emery and again rotated the same number of times, the process being repeated until the disc has been rotated 110 times. The loss in weight sustained by the sample is then measured and, if desired, further tests after 220, 330, or 440 revolutions may be made. The abrasion is measured by

$$\frac{S}{A}$$

where S is the loss in weight and A the area exposed to abrasion, or the loss in weight may be divided by the volume or weight of the sample.

F. B. O'Connor¹ has tested the resistance of floor tiles to abrasion by placing them in contact with a revolving table, 4 ft. diameter, revolving at 1500 revs. per hour, the table being supplied at a uniform rate with dry crushed quartz of 20–30 mesh. The tests were continued for 1 hour, several different pressures being applied, and after the conclusion of each test the thickness of the tile was measured in eight places and the mean taken.

M. L. Hartmann and J. E. Kobler² have tested the resistance to abrasion by cutting a groove in the ends of each brick to be tested so as to expose the maximum area to cutting and then applying the bricks at a constant pressure of 25 lb. for 5 minutes to a silicon carbide grinding wheel of grit 16, 12 in. diameter and with a 2-in. face, running at a constant speed (512 revs. per minute or 1560 ft. per minute). The depths of the groove before and after the test were measured; the

¹ *Trans. Amer. Ceram. Soc.*, 15, 233, 1913.

² *Amer. Electrochem. Soc.*, 37, 717–20, 1920.

difference represents in linear inches the abrasion during a 5 minutes' test. Results obtained by this test are shown in Table XIV.VIII.

C. E. Nesbitt and M. L. Bell¹ used a silicon carbide wheel, of grit 16, 18 in. diameter and 2 in. thick, revolving at 1640 ft. per minute. The sample was pressed against the wheel under a pressure of 100 lb. per sq. in. for 5 minutes and the depth of cut measured.

The *sandblast test* is typical of the methods in which the abrasive is projected on to the material to be tested. Various modifications of the test have been devised; that suggested by the U.S. Bureau of Standards is very convenient. The sample is weighed and then mounted with its face in a vertical position and immediately behind an iron plate in which is an aperture 6 cm. diameter, so that the area exposed to the action of the sand is 28.27 sq. cm. Standard Ottawa sand of 20–30-mesh is then projected on to the sample through a nozzle $\frac{1}{2}$ in. diameter at a pressure of 20 lb. per sq. in. for 3 minutes, the distance between the exposed face of the sample and the nozzle being 12 in. The effect of the sandblast is measured by the loss in weight during the test.

Aldred, Elliott and Cowling² have developed an apparatus to measure the Abradability Index which is very reproducible and is capable of general application. A regulated air blast projects a stream of graded fused alumina particles at the sample arranged so that it is at a fixed angle to the stream. A pre-determined weight of fused alumina particles (14 lb.) is used in each test and the Index is calculated by measuring the amount of specimen abraded and dividing this by its bulk density. The method has been adopted as a standard test by several laboratories and is known as the Morgan-Marshall Abrasion Test. The Abradability Index of some materials is given in Table XIV.IX.

Storey and Mackenzie³ have suggested that there is a relationship between the Abradability Index and the Modulus of Elasticity of refractory materials.

Emery and Bradshaw used a similar method with Standard Leighton Buzzard sand of 20–30-mesh projected from a nozzle 0.275 in. diameter at a pressure of 7 lb. per sq. in. for a period of 4 minutes, the surface to be tested being 7 in. from the nozzle.

Scratching tests are much older than abrasion tests, one of the earliest scales of hardness being that devised by Mohs, which is still in general use. It is based on the ability of a mineral to scratch one mineral in the series and to be scratched by the next harder mineral in the series. Mohs examined a large number of substances and selected ten, which he numbered according to their hardness, as shown in Table XIV.V, in which the hardness of a number of other substances is also shown.

The chief objection to Mohs' scale is that the minerals used as standards themselves vary in hardness to an appreciable extent, but it is very useful for preliminary tests. A series of substances of similar hardness may also be placed in the wrong order if variable pressure is applied when testing them. To overcome this difficulty, Turner⁴ made the scratches with a diamond attached to one end of a balanced lever

¹ *Metall. and Chem. Eng.*, 15, 205–212, 1910.

² Aldred, F. H., Elliott, A., and Cowling, K., *Trans. Brit. Ceram. Soc.*, 54, 239, 1955.

³ Storey, C., and Mackenzie, J., *Trans. Brit. Ceram. Soc.*, 56, 14, 1957.

⁴ *Proc. Birm. Phil. Soc.*, 5, Part II, 1886.

capable of moving vertically on a knife-edge and of being rotated. The lever is provided with a sliding weight and is graduated, so that each division of the scale corresponds to a weight of 10, 20, 30, or 40 grams at the diamond point. The sample to be tested is polished and is then tested by drawing it under the diamond point, whilst the latter is under various pressures, until a decided scratch is produced. The weight (in grams) on the point when this is effected is taken as a measure of the hardness. Martens modified this test by specifying that the scratch produced must be 0.01 mm. wide. This method was at one time used for measuring the hardness of metals, but it has not been extensively employed for ceramic materials.

TABLE XIV—IX
ABRADABILITY INDEX OF SOME CERAMIC MATERIALS.

<i>Material</i>	<i>Abradability Index</i>	<i>Material</i>	<i>Abradability Index</i>
Fused basalt tiles	34	Fireclay bricks (22% porosity)	80—120
Vitreous fireclay tiles	36—37	Insulating Refractory Concrete	90—140
Red flooring tiles	43—56	Silica bricks	70—100
Dense fireclay bricks	50—65	Carbon bricks	130—180
Molochite blast furnace bricks	45—55	Insulating fireclay bricks	200—300

More accurate comparisons of hardness can be obtained by measuring the size of the indentation produced, but for this purpose a 'scratch' is not so convenient as a circular indentation.

Indentation tests are based on the assumption that the volume of an indentation is proportional to the softness of the material. The particular form of this known as the Brinell Test has been very largely used for testing steel and other metals. In its simplest form it consists in measuring the depression caused by a steel ball applied directly to the material. In the form modified by Le Chatelier and B. Bogitch¹ to make it applicable to ceramic materials, a piece of thin lead foil, 0.05 mm. thick, previously blackened by the action of sulphuretted hydrogen in slightly acid solution and then dried and smeared with vaseline which is largely removed again, so as to leave a matt surface, is laid on the surface to be tested, and on this is placed a hardened steel ball, 17.5 mm. diameter. A pressure of 500 kg. is applied to the ball for exactly 60 seconds, after which the depth or the diameter of the indentation is measured. The hardness is then calculated from the formula:

$$H = \frac{P}{1.5708D(D - \sqrt{D^2 - d^2})}$$

where H is the hardness, P the pressure in kg., D the diameter of the sphere, and d the diameter of the indentation. It may also be calculated from the formula:

$$H = \frac{P}{3.1416De}$$

where e is the depth of the indentation and is equal to $\frac{1}{2}(D - \sqrt{D^2 - d^2})$.

¹ *La Céramique*, 371, 17-18, 1919.

For hard materials, a pressure of 3000 kg. is usually required, but for softer ones 500 kg. is sufficient. The results obtained by the use of different weights are not strictly comparable, so that, as far as possible, a constant weight should be employed.

When testing metals, no foil is used, but it is essential with most ceramic materials, as otherwise the indentation is not clearly defined.

A modification of the Brinell test was used for testing the hardness of glazes by G. Blumenthal, jun.,¹ who allowed a hardened, rounded tungsten-steel point to bear on the glaze surface for 3 minutes under a pressure of 50 lb. and then measured the diameter of the indentation. The hardness was calculated from the formula given above.

E. Rengade and E. Desvignes² measure the hardness of refractory materials at high temperatures by supporting a cylindrical test-piece on a graphite block in an electric furnace of the Rosenhain type and pressing upon it a 90° cone by means of an amplifying lever applied through a rod of Acheson graphite, the depth of penetration being measured by a rule shaped at the end to fit the hollow formed by the cone.

In the *Shore scleroscope*, a hardened steel cylindrical hammer about $\frac{1}{4}$ in. diameter and $\frac{3}{4}$ in. long, with a striking tip about 0.02 in. diameter and weighing about $\frac{1}{12}$ oz., is allowed to fall through a glass tube from a height of 10 in. on to the material to be tested. The height of the rebound is measured on a scale and the hardness calculated from the figure so obtained. Although the scleroscope is regarded as measuring the hardness of a material it does not really do so, but only the elasticity; it does not give very concordant results with ceramic materials and is not used to any great extent, the modified Brinell test being more suitable.

MINOR PROPERTIES

Ring. The clear ringing note or 'ring' which some burned ceramic materials emit when struck is often a good indication of the extent of the burning and the absence of cracks. A dull 'ring' is usually due to the presence of small cracks, some of which may cause serious trouble if used under exacting conditions, whilst others are so minute as to be of little or no importance. The note emitted by silica bricks made from pre-calcined quartz is much duller than that from bricks made from the raw material; the difference is probably due to extremely minute cracks in the individual grains.

Whilst of considerable use as a rough test, too much reliance must not be placed upon the sound emitted when a sample is struck, because the note depends on so many factors, some of which may affect the 'ring' without being necessarily harmful. **Feel.** Most ceramic materials and many others have a characteristic 'feel', which may be (a) smooth, (b) rough, (c) meagre or harsh, (d) greasy, soapy, silky, or unctuous. Most refractory materials belong to the first three groups, but many clays are included in the last one. Some materials may be classed in two groups simultaneously; thus, china clay and dry ball clay are smooth and unctuous; many fire-clays feel 'rough', but a freshly-cut surface, when rubbed with the fingers, has a

¹ *J. Amer. Ceram. Soc.*, 4, 896, 1921.

² *Chaleur et Industrie*, 3, 965, 1922.

slightly greasy feel. As the tongue is often more sensitive than the fingers, it has long been the custom to compare some fine clays by placing a small portion in the mouth and 'working' it with the tongue. By this means the presence of a very small proportion of grit in an otherwise impalpable material is readily recognised.

Experts can readily distinguish different varieties of porcelain and other ware by the 'feel', and this property is often very useful as a supplementary indication of the nature of a material.

Odour. Many clays, when moist, have a characteristic earthy odour, which probably is due to carbonaceous matter present, as it can be removed by treatment with a solution of iron saccharate, the odour being transferred to the latter. When the clay is heated to redness, the characteristic odour is lost. Impurities may sometimes be detected by the odour they emit, especially when heated. Thus, some clays and alum shales have a sulphurous odour on account of the pyrites present in them. This is particularly noticeable when the clay is freshly cut or heated to redness in a closed vessel.

Sectility and Fissibility are two closely related terms, indicating that a material to which they are applied can readily be cut, in at least one direction. Shales are of this character, though the 'cutting' is possibly more in the nature of 'splitting', or separating the existing laminae of which the material is composed. In order to be sectile a material must usually be moderately soft, but a hard material composed of thin sheets united by a soft cement will be fissile in a direction parallel to the sheets.

The most sectile clays are ball and china clays when almost dry, and also some of the surface clays. Harder or leaner clays are friable rather than sectile, so that when a knife is applied to them they are crushed rather than cut.

Most ceramic materials lose their sectility when heated to redness, but this property is retained to a large extent by certain rather soft bricks (known as *cutters*), and by many tiles.

In raw clays, sectility is usually associated with a fine texture and a low proportion of sand, but in the burned products this property is due to the large proportion of sand present and to the heat-treatment and temperature attained in the kiln being insufficient to produce a very strong bond. It is important with such articles, as it enables the brick- or tile-layer to cut them to different sizes in order to fit them into special places. It may be noted that silica bricks are more difficult to cut than those made of fireclay, chiefly on account of their coarser texture and greater brittleness.

Friability may be regarded as the converse of resistance to abrasion; it is considered more fully in Chapter XIII.

Acoustics and Sound Absorption. Although the walls of most dwelling houses are built of stone or bricks and the interior ones are covered with plaster they are not efficient absorbents of sound—seldom absorbing more than about 3 per cent of the sound reaching their surface. Thus brickwork walls 9 in. thick will allow conversation to be heard through them but it is seldom intelligible to the listener. Walls $13\frac{1}{2}$ – $31\frac{1}{2}$ in. permit sound to be transmitted to the extent that a noise can be heard but conversation is unintelligible unless the voices are raised. It requires brick walls at least 36 in. thick to render conversation on one side wholly inaudible on the

other. Hollow blocks tend to transmit sounds much more readily than solid walls as the insulation of sound depends chiefly on the mass of the insulator.

In sound-insulation the structure, rigidity and hardness of the surface are the most important factors and non-ceramic materials can provide these more effectively than ceramic ones.

THERMAL PROPERTIES

MANY of the thermal properties of ceramic materials have been described in Chapter XII, in connection with the physical changes which are brought about by the effect of heat. There are three other important thermal properties of materials which are important in ceramic practice; these are (a) the thermal capacity or the specific heat, (b) the thermal conductivity and diffusivity, and (c) the thermal shock resistance.

THE THERMAL CAPACITY OR SPECIFIC HEAT

VARIOUS materials appear to have different capacities for heat, i.e. equal masses of different substances which are all at the same temperature absorb different quantities of heat before they are raised to a given temperature. The ability of a substance to absorb and retain heat is termed the thermal capacity of that substance, and in order to compare the thermal capacities of different substances a standard of measurement is used, termed the *specific heat*, which may be defined as the amount of heat required to effect an increase of one degree in the temperature of unit mass of the substance under a definite pressure (usually one atmosphere). For convenience the specific heat of water is assumed to be unity, and other substances are expressed in relation to this.

The physical explanation of the specific heat of a pure crystal is afforded by a study of the forces acting between adjacent atoms or ions in the lattice. As Fig. XIV.1 shows, there is a certain separation distance a between ions in a crystal lattice at which the forces of attraction and repulsion exactly balance. As they approach one another more closely, repulsion forces tend to restore the equilibrium position, as do attraction forces when the separation distance becomes greater than a . There is, however, a small distance through which the ions vibrate and this becomes greater as the temperature increases, but in this process heat is absorbed equivalent to the amount of energy expended. Those crystals in which the resultant force line, Fig. XIV.1, is steeply inclined in the neighbourhood of the equilibrium position will absorb more energy in vibrating over a certain distance than those where the resultant force line is less steep. So when heated through a certain temperature range some crystals absorb more heat than others, i.e. their specific heat is greater.

Crystals with the greatest specific heat are those in which the ions are close-packed and those in which the cations and anions have widely-different electro-negativities (Chapter II).

The specific heat depends on whether the substance is in the crystalline or glassy state, or, if the former, what is its crystalline form and internal molecular arrangement. Thus, crystalline quartz has a specific heat of 0.185 between 12° and

100° C., whilst the specific heat of amorphous silica (opal) between 12° and 100° C. is 0.2375.

The specific heat is not constant at all temperatures, so that it is necessary to specify the particular rise in temperature employed in the definition; this may be from 0°–1° C., 32°–33° F., 60°–61° F., or any other convenient range. The temperature should be stated in any report of the results.

The specific heat is usually fairly constant between 10° C. and 200°–300° C., but boron, carbon, and silicon are exceptions, and vary very greatly between these temperatures. At higher temperatures the specific heat of ceramic materials increases somewhat more rapidly than the corresponding rise in temperature.

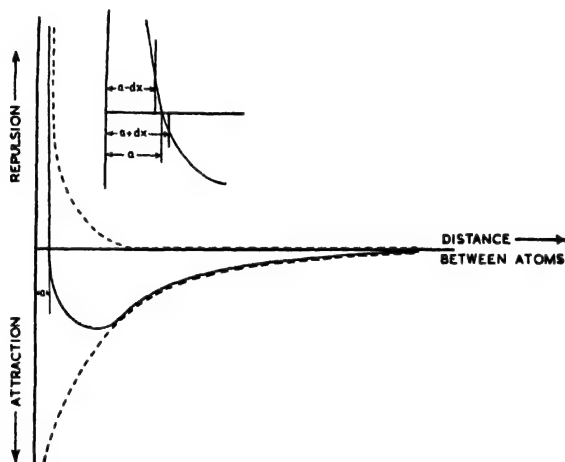


FIG. XIV.1. THE FORCES OF REPULSION AND ATTRACTION BETWEEN ADJACENT ATOMS IN A CRYSTAL

The resultant is shown as a solid line

Vogt has stated that the specific heat at different temperatures may be calculated from the formula:

$$C_t = C_0(1 + 0.000078t)$$

where C_t is the specific heat at temperature t ° C., and C_0 is the specific heat at 0° C.

The specific heat of substances is generally greater when they are in the liquid than in the solid and gaseous states.

The specific heat of kaolin over the range 0°–1000° C. averages 0.5, and that of ball clay 0.45; for smaller ranges above 1000° C. it tends to be about 0.2.

A determination of the specific heat of a substance is usually made by means of the method of mixtures,¹ by heating a weighed quantity of the substance to the required temperature for some time until it is uniformly heated. It is then quickly transferred to a suitable calorimeter containing a weighed quantity of cold water at a

¹ Cf. Cohn, W. M., *J. Amer. Ceram. Soc.*, 10, 347, 1927.

known temperature, and the latter is stirred so as to distribute the heat. The temperature of the water is noted at intervals of half a minute or so, until a constant temperature is reached. The specific heat is then calculated from the following formula:

$$\text{Specific heat} = \frac{W_2 \times (T_3 - T_2)}{W_1 \times (T_1 - T_3)}$$

where W_1 is the weight of the substance in grams.

W_2 is the weight of the water in grams.

T_1 is the maximum temperature of the substance.

T_2 is the original temperature of the water.

T_3 is the final temperature of the water.

The above formula is based on the assumption that the quantity of heat in the substance at the given temperature is $W_1 T_1 s$, where W_1 and T_1 have the same significance as in the formula and s is the specific heat at the temperature T_1 .

The heat in the water prior to the determination is $W_2 T_2$, and after the determination it is $W_2 T_3$, and as the whole of the heat lost by the substance is assumed to be transferred to the water $W_1(T_1 - T_3)s = W_2(T_3 - T_2)$.

Where accurate results are required, a special calorimeter must be used and numerous precautions taken to avoid the loss of heat by radiation. This is especially necessary in the case of substances having a low thermal conductivity, which take a considerable time before they are cooled to a constant temperature.

The **atomic heat** of a solid substance is the product of its specific heat and atomic weight, and it has been found by Dulong and Petit that for elementary substances the atomic heat is nearly constant, viz. 6.2–6.3, though this does not appear to apply to some elements with atomic weights of less than 40. According to more recent investigations, 5.9 is a more reliable figure for the atomic heat at constant volume and 6.2 for that at constant pressure.¹

Boltzmann² has shown that the atomic heat can be directly deduced from the classical Kinetic theory, and that the constant of Dulong and Petit should be 5.97.

The heat capacity of ceramic materials is often very important and especially when they form part of the walls of furnaces, etc., as all the heat absorbed by such material is, in a sense, wasted and ought to be used in heating the contents of the furnace.

The specific heat of most materials increases with the temperature, so that the fuel consumption when heating ceramic materials at high temperatures is much greater than at low temperatures, the same weight of material being used in each case. Thus, in fireclay bricks, according to Bradshaw and Emery,³ the relation between the fuel consumption at 1200°–1400° C. and that at 100°–300° C. is nearly 3:2.

Clays. J. M. Knoté⁴ found the specific heat of raw clay to be about 0.237, that of clay heated to 650° C. 0.204, and that burned at 1050° C. to be 0.200 C.G.S. units.

¹ *Physical Chemistry for Colleges* (M'Graw-Hill Book Co., 1921).

² *Sitzb. Kgl. Akad. Wiss. Wien.*, 63 (2), 679, 1871.

³ *Trans. Eng. Ceram. Soc.*, 19, 88, 1919–20.

⁴ *Trans. Amer. Ceram. Soc.*, 14, 394, 1912.

It will be seen that the dehydration of clay causes a decrease in the specific heat. The specific heat at 1050° C. is practically the same as that at 650° C., the difference being due probably to the water not completely removed during the decomposition at 650° C. The specific heat of kaolin at different temperatures is shown in Table XIV.X.

TABLE XIV—X. CHANGES IN SPECIFIC HEAT OF KAOLIN

<i>Temperature, ° C.</i>	<i>Specific Heat</i>
—	0.235
22–98	0.2242
440–1000	0.235
650	0.204
1050	0.200

The specific heat of *fireclay bricks* at different temperatures may, according to S. T. Wilson and A. D. Holdcroft,¹ be calculated from the formula:

$$\text{Sp. ht.} = 0.193 + 0.00006t$$

where t is the temperature in ° C., but Bradshaw and Emery² have found that the specific heat of fireclay bricks at different temperatures is more correctly shown by the formula:

$$0.193 + 0.000075t$$

where t is the temperature in ° C. This is about 25 per cent higher than Wilson and Holdcroft's figure.

Table XIV.XI shows the specific heats of various materials between 25° and 1400° C.

TABLE XIV—XI. SPECIFIC HEATS OF VARIOUS BRICKS

<i>Temperature ° C.</i>	<i>Building Brick</i>	<i>Silica Brick</i>	<i>Firebrick</i>	<i>Zirconia Pure</i>	<i>Magnesite</i>	<i>Carbon</i>
600	0.216	0.228	0.228	0.137	0.291	0.377
1000	0.253	0.262	0.265	0.157	0.324	0.412
1200	—	0.283	0.284	0.167	0.340	—
1400	—	0.295	0.297	0.175	—	—

Porcelain. The specific heat of unglazed Berlin porcelain is, according to W. Steger, 0.202 C.G.S. units, between 20° and 200° C. and 0.221 between 200° and 400° C.

Siliceous Materials. Table XIV.XII, due to W. P. White, shows the specific heat of various forms of silica.

¹ *Trans. Eng. Ceram. Soc.*, 12, 279, 1913.

² *Loc. cit.*, p. 655.

TABLE XIV—XII. SPECIFIC HEAT OF VARIOUS FORMS OF SILICA

Temperature ° C.	Quartz Glass	α -Quartz	β -Quartz	Cristobalite
100	0.202	0.204	—	—
250	0.236	0.244	—	—
500	0.266	0.294	—	—
550	—	0.313	—	—
750	0.280	—	0.277	0.278
1000	0.290	—	0.288	0.285
1100	—	—	—	0.287

The specific heats of silica and fireclay bricks are very similar, generally about 0.26. The specific heats of various silicates are shown in Table XIV.XIII.

TABLE XIV—XIII. SPECIFIC HEAT OF VARIOUS SUBSTANCES

Temperature	Pseudo-Wollastonite	Wollastonite	Orthoclase	Diopside	Quartz	Orthoclase Glass	Soft Glass
100	—	0.1833	—	0.1919	0.1840	—	0.1977
500	0.2159	0.2180	0.2248	0.2310	0.2372	0.2291	0.2400
700	—	0.2286	—	0.2420	0.2547	—	0.2646
800	—	—	0.2401	—	—	0.2465	—
900	—	0.2354	—	0.2499	0.2597	—	0.2791
1100	0.2380	0.2423	0.2505	0.2562	0.2643	0.2588	0.2907
1300	0.2422	—	—	0.2613	—	—	0.2945
1500	—	—	—	—	—	—	0.2999

The increase in the specific heat of a material at high temperature is very noticeable.

Barus gives the specific heats of solid and molten diabase as shown in Table XIV.XIV.

TABLE XIV—XIV. EFFECT OF FUSION ON SPECIFIC HEAT

Temperature	State	Specific Heat
800°–1100° C.	Solid	0.304
1200°–1400° C.	Liquid	0.350

The specific heats of various silicates, etc., present in bricks naturally modify the total specific heat, but they are usually present in such small quantities that they do not cause any appreciable difference in the specific heat of the material.

Alumina has a specific heat (according to Russell¹) of 0.200 between 3 and 48° C. and, according to G. B. Wilkes² it rises from 0.206 to 0.280 between 100° C. and 1700° C., in a smooth parabolic curve.

¹ *Phys. Zeit.*, 13, 59, 1913.

² *J. Amer. Ceram. Soc.*, 15, 72, 1932.

Lime has a specific heat of 0.113 between 0° and 150° C.

Magnesia has a specific heat of 0.258 to 0.340.¹

Zirconia has a remarkably low specific heat; Holdcroft and Mellor give the figures for its value at different temperatures as shown in Table XIV.XI.

Carbon bricks have a specific heat of about 0.312 at 200° C. and 0.412 at 1000° C.

THE TRANSMISSION OF HEAT

WHEN the surface of a body is heated, the rise in temperature is not restricted to the external layer, but the heat is transmitted through the mass. Similarly, if a hot body is placed in contact with a colder one, heat is transferred to the latter.

The transmission of heat from one body to another may be effected in various ways:

(a) By **conduction**, in which the heat is transferred by molecules of the hotter substance bombarding those of the cooler substance and so setting up a corresponding motion amongst the molecules in the latter, which were moving less rapidly; the acceleration of motion progresses at a definite rate through the second substance. The ease at which the heat passes through a material—as measured by the rise in temperature of the latter—is termed *thermal conductivity*.

As a result of their different atomic structures, materials have different powers of conducting heat. Most metals have a higher thermal conductivity than non-metals or compounds, i.e. they conduct heat rapidly through their mass. Ceramic materials are, on the whole, very poor conductors of heat, though some, such as silicon carbide, have a higher thermal conductivity than others.

The fundamental equation governing the conduction of heat may be expressed as:

$$Q = -kA \frac{dT}{dx}$$

where Q is the amount of heat flowing through a body of cross-sectional area A , and dT/dx is the temperature gradient in the direction perpendicular to A .

(b) **convection**, in which the heated particles move away from the hotter to the cooler parts of the mass and carry 'heat' with them. Convection can only occur in fluids, as the particles in a solid are not sufficiently mobile.

(c) **radiation**, in which the heat is carried neither by conduction nor convection, but in a manner comparable to the transmission of light. Heat may be radiated instantaneously through space as well as through air and other gases, and when so radiated it scarcely affects the temperature of the medium through which the 'rays of heat' are passed. There is a very close relationship between radiated heat and light. Both can be reflected by mirrors and deflected or refracted by prisms and lenses; in fact, the chief difference between them appears to lie in the difference in wavelength.

Hence, when a body is sufficiently heated, the heat rays emit a form of light and the body is said to be 'incandescent'. When heat rays are absorbed by any substance

¹ According to Wilkes (loc. cit.), between 100° C. and 1800° C. the specific heat rises from 0.2335 to 0.2945 in a smooth parabolic curve.

the latter is heated and its temperature increased in proportion to the amount of heat absorbed, but the air through which the heat rays pass may remain at a much lower temperature. This is due to the fact that radiated heat is absorbed more by some surfaces than others, the nature of the surface being of greater importance, in this respect, than the composition of the heat absorbing material. Similarly, the amount of heat radiated from a body varies according to the colour and nature of the radiating surface, being low for polished metal and high for rough, black surfaces. In the latter, it is proportional to the fourth power of the absolute temperature:

$$E = k(T_1^4 - T_0^4)$$

where E denotes the radiation from a body at T_1 , to one at T_0 and k is a constant. The radiation loss, apart from convection, is usually (for a temperature difference of 100°C.) 0.015 gram-cal. per second for each cm. of heat-radiating surface.

Factors Influencing Thermal Conductivity. The chief factors to be considered in connection with the rate of passage of heat through ceramic materials are:

- (a) The chemical composition of the material used.
- (b) Its previous heat treatment.
- (c) The texture or physical condition of the material.
- (d) The porosity of the material and the sizes and distribution of the pores.
- (e) The temperature at which the material is used or tested.

Thermal conductivity is a property which is, as yet, not fully explained on the basis of theoretical reasoning. Debye¹ considers that the atomic or ionic groupings within a crystal act as oscillators or vibrators and if these frequencies correspond to those of the thermal waves, conduction will readily proceed. On this basis, highly symmetrical crystals where the vibrations are harmonic will be better conductors of heat than those which are disordered or contain many types of bond. Whilst this simple concept applies in general terms, there are many discrepancies in experimental findings which suggest that other factors are involved.

Materials differ with regard to their thermal conductivity, which also changes with the heat treatment to which they have been subjected, just as the temperature and duration of firing during manufacture modifies other properties of such materials. It is also important to know the condition of the material during use, as the thermal conductivity of a brick or block may be quite different from that of the same substance when in the powdered state. Thus, magnesia when in the form of a refractory brick is a moderately good conductor of heat, whilst in the form of a powder it is extremely resistant to heat and has a high insulatory value.

The influence of texture and porosity may be considered together, as the principal effect on the thermal conductivity is due to the relation between the amount of solid and of air which the heat has to traverse in passing through the material. As air is a much better insulator than any solid material, the larger the proportion of air the greater will be the thermal insulating power of the material. Hence, a fine-grained, close-textured material has a much greater thermal conductivity than one with a coarser open texture. The relation between insulating power and texture or porosity cannot, however, be expressed in very simple terms, as it is modified by

¹ Debye, P., *Amer. Physik.*, 39, 789, 1912.

(a) temperature, (b) the size, and (c) the shape of the pores or interstices, (d) the position of the interstices relative to each other and to the solid matter.

If the rate of radiation increases until it equals the rate of conduction through a solid the pore spaces will cease to act as insulators. With pores 0.01 cm. diameter this equality of heat transfer occurs, according to Dougill, Hodsman and Cobb,¹ at 3600° C. At lower temperatures, or with wider pores, the rate of radiation is lower than that at which the heat passes through the solid material, so that the presence of pores in materials used at any temperature ordinarily attainable decreases the thermal conductivity.² A. T. Green³ has, however, stated that at much lower temperatures (e.g. 1400°–1500° C., and even at 1150° C.) some of the pore spaces lose their insulating properties and transmit heat at nearly the same rate as the solid matter. If this statement is correct, pore spaces in ceramic materials do not have so great an insulating power at high temperatures as is usually assumed.

An important distinction must be made between open and closed pores (see p. 397), because the former permit the passage of hot gases and thus may increase the effective thermal conductivity. A permeable brick is invariably not as good in thermal insulation characteristics as a non-permeable one of the same porosity.

In comparing the thermal conductivity of different substances, the unit is the amount of heat which passes in one second through a mass of the material of unit thickness and area when the difference in temperature of opposite faces is one degree. If the C.G.S. unit is adopted the thermal conductivity will be expressed as gram-calories per second per sq. cm. of material 1 cm. thick for a temperature-difference of 1° C. The British Unit of thermal conductivity is the number of B.T.U. per second per sq. in. for material 1 in. thick for a temperature-difference of 1° F. Another convenient British Unit is the B.T.U. transmitted per sq. ft. of material 1 in. thick in one hour for a temperature-difference of 1° F.

The smaller British unit can be obtained by dividing the conductivity in C.G.S. units by 178 and the larger British unit by multiplying the C.G.S. figure by 2903.

The reciprocal of thermal conductivity or resistance offered by unit mass of a substance to the passage of heat is termed its *resistivity* or *insulating power* (p. 862).

The thermal conductivity of a solid substance, such as a ceramic material, is usually determined by exposing one face to a constant source of heat and measuring the temperature at opposite faces, or at the hot face and at a point in the material a convenient distance from it. The greatest source of error occurs in applying the heat uniformly to the hot face and ensuring its uniform distribution through the material to be tested, so the various methods which have been devised for determining the thermal conductivity differ in the means used to avoid this source of error.

In Wologdine's method,⁴ the test pieces are in the form of round flat plates, 160 mm. (6.4 in.) diameter and 50 mm. (2 in.) thick. Holes are pierced to depths of 5 mm. (1.2 in.), 45 mm. (1.8 in.), and 50 mm. (2 in.) from the upper surface and

¹ *J. Soc. Chem. Ind.*, 34, 465, 1915.

² There are some exceptions to this statement.

³ *Trans. Eng. Ceram. Soc.*, 21, 394, 1921–22.

⁴ *Bull. Soc. Encour.*, 3, 879, 1909.

thermo-couples attached to pyrometers inserted in them. The lower surface of the test piece is heated in a gas furnace and the heat passing through it is measured by a water calorimeter, whilst the temperature at each of the levels above mentioned is read at intervals.

The heat passing through the plate may be calculated from the formula:

$$Q = \frac{P(t_2 - t_1)}{60}$$

where Q is the quantity of heat traversing per second an area equal to that of the base of the calorimeter, t_1 and t_2 the temperatures of the water entering and leaving the calorimeter, and P the quantity of water passed in grams per minute. The coefficient of thermal conductivity is

$$\frac{S(T_5 - T_0)}{QL}$$

where S is the area of the bottom of the calorimeter in square cm., L the thickness of the plate in cm., and T_0 and T_5 the temperatures of the upper and lower surfaces.

Modern methods of measuring the thermal conductivity of whole bricks or slabs of material are based essentially on Wologdine's method, although considerable modifications in experimental details have been introduced. The principal source of error in such measurements is in the loss of heat from the sides and ends and in a rectangular-shaped specimen these cannot be eliminated entirely. They can be minimised, however, by employing large, flat specimens and providing an insulated surround.

A method commonly used in English practice is based on the apparatus developed by Blakeley and Cobb.¹ The design is shown in Fig. XIV.2.

For the purposes of the test, a whole brick (9 in. \times 4½ in. \times 3 in. or 2½ in.) is used. It is placed face downwards on an electric heater comprising a flat steel or brass plate fitted over a tile wound with resistance wire or tape. The top surface of the brick is covered with a blackened metal plate into the centre of which is fitted a thermocouple T_3 . Further thermocouples (T_2) are placed on the upper surface and (T_1) beneath the lower surface of the brick in contact with the heater plate and it is advisable to recess this into the brick, otherwise there may not be contact between the brick and heating element at all points.

The brick and heater assembly is enclosed in a box lined with diatomite blocks, and diatomite or alumina powder filled into the gap between the brick and the box.

A steady current is applied to the heater element and measurements of the temperature on the top and bottom faces of the brick (as indicated by the thermocouples T_2 and T_1) and measurement of T_3 (to indicate the heat loss) should be taken when they have reached a constant value. As the thickness of the brick and the temperature gradient across it are known, the thermal conductivity can be calculated. Determinations of the conductivity at various hot face temperatures can be carried out by regulating the current supplied to the heater.

¹ Blakeley, T. H. and Cobb, J. W., *J. Soc. Chem. Ind.*, 51, 237, 1932.

The American Society for Testing Materials (1947)¹ has adopted the method described by Norton in 1942.² The heating element must be capable of giving a hot face temperature over the range 400°–2800° F. and be equipped with controlling devices to ensure a constancy of $\pm 5^\circ$ F. A water calorimeter is employed to measure heat flow and end losses are reduced by using similar bricks along the sides of the test brick and soap bricks against the end faces.

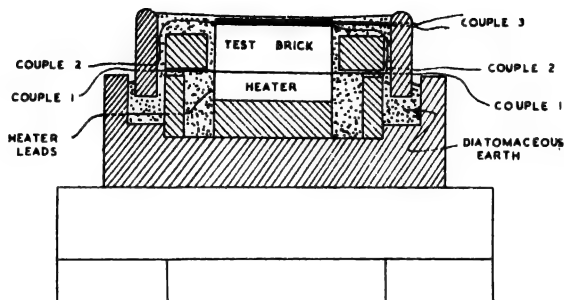


FIG. XIV.2. AN APPARATUS FOR MEASURING THE THERMAL CONDUCTIVITY OF CERAMIC MATERIALS

For more accurate determinations of the thermal conductivity and entirely eliminating end effects, it is better to use a specimen which completely surrounds the heat source. Adams and Loeb³ have described a highly satisfactory apparatus using a specimen in the form of a prolate spheroid moulded round a heater core. Kingery⁴ has used spherical and cylindrical specimens.

Thermal conductivity measurements are made after equilibrium in the heat flow conditions have been attained and take no account of the rate at which heat flows through the material. This latter property is the *Thermal Diffusivity* which may be defined as the rise in temperature produced in 1 cc. of the substance by 1 calorie acting during 1 second through 1 sq. cm. of a layer 1 cm. thick, having a temperature difference of 1° C. between its faces.

The coefficient of diffusion is represented by:

$$\frac{K}{dh}$$

where K is the amount of heat in gm.-cals. which is transmitted in 1 second through a plate 1 cm. thick per sq. cm. of its surface when the difference in temperature between the two sides is 1° C., d is the specific gravity, and h the specific heat of the material.

A. T. Green⁵ has found the average temperature-diffusivity of six silica products to be those shown in Fig. XIV.3; the thermal conductivity of the same

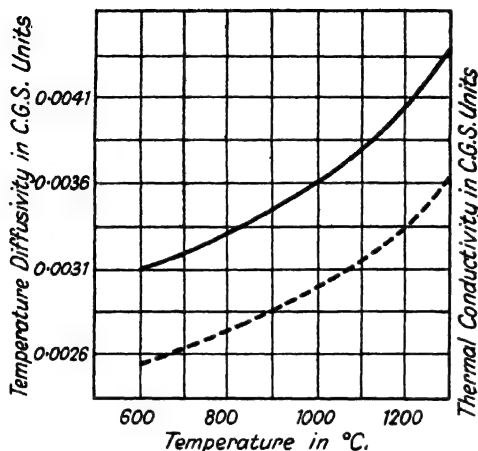
¹ A.S.T.M., Designation C.201-47.

² Norton, F. H., *Refractories*, 2nd edn. (McGraw-Hill, New York, 1942).

³ Adams, M. and Loeb, A. L. *J. Amer. Ceram. Soc.*, 37, 73, 1954.

⁴ Kingery, W. D., et al., *J. Amer. Ceram. Soc.*, 37, 67, 1954.

⁵ *Trans. Ceram. Soc.*, 26, 171, 1926-27.



Average for six Silica Products —————
 Average for six Fireclay Products - - - - -

FIG. XIV.3. TEMPERATURE/THERMAL DIFFUSIVITY CURVES OF SILICA AND FIRECLAY PRODUCTS

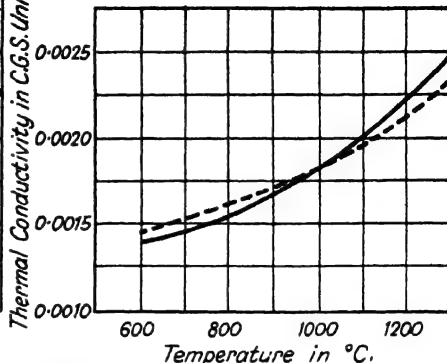


FIG. XIV.4. TEMPERATURE/THERMAL CONDUCTIVITY CURVES FOR SILICA AND FIRECLAY PRODUCTS

materials is shown in Fig. XIV.4. Individual materials differ so greatly from the average that no comparison in general terms is very reliable.

The coefficient of thermal conductivity (K) at $t^\circ \text{C}$ is

$$K = kcs$$

where k is the coefficient of thermal diffusivity at $t^\circ \text{C}$, c the apparent density, and s the true specific gravity at $t^\circ \text{C}$.

Fourier's law for the linear flow of heat is:

$$\frac{d\theta^2}{dx^2} = k \frac{d\theta}{dt}$$

where θ denotes the temperature, x the distance from a hot surface, t the time and k the diffusivity. Calculations based on this formula, made by Heyn, Bauer and Wetzel, give much lower results for conductivity than those obtained by means of calorimeters.

Thermal diffusivity apparatus is difficult to design but can be based on the standard conductivity equipment. Two special techniques have been described in recent years; the first due to Fitzsimmons¹ involves immersing the specimen in a lead bath and measuring the rate of rise of temperature at the centre of the body; Van Zee and Babcock² have measured the thermal diffusivity of molten glass by superimposing a small temperature variation (58°C .) on the mean temperature of

¹ Fitzsimmons, E. S., *J. Amer. Ceram. Soc.*, 33, 327, 1950.

² Van Zee, A. F. and Babcock, C. L., *J. Amer. Ceram. Soc.*, 34, 244, 1951.

the sample which could be maintained at several points between 700°–1400° C. The amount of time taken for the impulse to travel to the centre of a cylindrical specimen was judged to be a measure of the diffusivity.

Emissivity is defined as the amount of heat or other energy radiated or absorbed by a substance; that emitted by an ideal black body being taken as unity.¹ To be truly comparable the surface of the ceramic body should be polished. Black and dark coloured surfaces have higher emissivities than white or light coloured ones; at 1000° C. chrome bricks have an emissivity of 0.98 units² whilst fireclay bricks³ and silica bricks⁴ have an emissivity of 0.55–0.6 and a brick containing 91 per cent of alumina⁵ has an emissivity of 0.75; silicon carbide bricks also have an emissivity of 0.75 at that temperature.

According to A. Schmidt at about 38° C. the radiation and emissivity of red brick and porcelain are:

	<i>Radiation</i> C.G.S. units	<i>Emissivity</i> (Black body = 1)
Red brick	4.61	0.94
Glazed porcelain	4.58	0.94

Thermal conductivity, diffusivity and emissivity are all of importance to users of ceramic materials.

For example, the loss of heat through a furnace wall is given by the expression:

$$H = K(T_1 - T_0) \frac{S}{l}$$

where H represents the flow of heat, T_0 the temperature of the cold or outer surface, T_1 that of the hot or inner surface of the wall, S the area, l the thickness, and K the mean thermal conductivity between the temperature T_0 and T_1 .

If s is the inner area of the wall and S the outer area, the geometric mean is \sqrt{sS} and

$$H = K(T_1 - T_0) \frac{\sqrt{sS}}{l}$$

In electrical furnaces the term *thermal mho* is generally used to express in watts the heat radiated in gm.-cals. per second per cm. cube for a difference of 1° C., a watt being equivalent to 0.2388 calories per second. The reciprocal value of this, the *thermal ohm*, represents the difference of temperature divided by the flow of heat in watts per cm. cube.

The thermal conductivity expressed in C.G.S. units may be converted into thermal ohms by multiplying the reciprocal of the conductivity by 0.2388. To reduce gm.-cals to watts, the reciprocal of the conductivity is multiplied by 4.186. The watts may be resolved into power as follows:

¹ The radiation of an ideal black body is assumed to be 4.9×10^{-8} kilo-calories per sq. m. per hour per °K⁴. In furnaces and kilns working under normal conditions and with the doors closed, the radiation from the walls and contents conforms broadly to that of a hot black body.

² R. H. Heilman, *Trans. Amer. Inst. Chem. Eng.*, 31, 165, 1934.

³ L. R. Barrett, *Trans. Brit. Ceram. Soc.*, 48, 235, 1949.

⁴ A. Baritel, *Chal et. Indust.*, 19, 237, 299, 1938.

⁵ A. Schmidt, *Stahl u Eisen*, 1927, p. 1336.

$$\text{Watts} \times 0.0013411 = \text{horsepower}$$

$$\text{Watts} \times 0.0568776 = \text{B.T.U. per minute}$$

$$\text{Watts} \times 0.0143329 = \text{calories per minute}$$

Contact conductivity, or rather its reciprocal, contact resistance, which is denoted by R , represents the difference in temperature in $^{\circ}\text{C}$. between the hot body and the surrounding medium, divided by the number of watts or gram-calories per second which flows from each sq. cm. of surface.

$$R = \frac{36,000}{2 + \sqrt{v}}$$

when v denotes the velocity of air (which results from the temperature difference) in cm. per second, and the loss of heat per sq. cm. surface per second for a difference in temperature of $t^{\circ}\text{C}$. will be

$$\frac{t}{R} \text{ cal. per second}$$

The thermal conductivity is a very important property in ceramic materials. Thus, the walls of a furnace which is internally heated are required to have a low thermal conductivity so that as little heat as possible will be lost through them. The walls of a muffle, retort, saggar, or similar appliance, on the contrary, must have a high thermal conductivity in order that the heat may pass through them in order to heat their contents.

Effect of Heat on Thermal Conductivity. The effects of heat on the thermal conductivity of ceramic materials and the various other equivalents of this property, such as resistivity, diffusivity, etc., are very important when the materials are required to act as heat insulators and prevent the escape of heat from furnaces, etc., or as conductors which allow heat to pass through them from a source of heat situated on one side or externally to the article or materials to be heated on the other side or internally. The use of heat insulators is typified in the case of furnaces and kilns of all kinds, as the heat is required to be applied to their contents and not allowed to escape unnecessarily to the open air. The use of ceramic materials as thermal conductors is typified by their employment as retorts, muffles, saggars, or crucibles, the contents of which are heated, but all flames, etc., being arrested by the ceramic material.

The rate at which heat passes through ceramic materials may be expressed in different ways, according to the purpose for which they are used.

Conclusions and deductions based on the thermal conductivity or resistivity of a ceramic material must be used with great caution, as various other factors may require to be taken into consideration. For instance, the thermal conductivity of firebricks used under oxidising conditions is quite different from that when the same bricks are employed under reducing conditions; in the latter case they may quickly become coated with a layer of carbon ('retort graphite') which entirely alters their behaviour with respect to the transmission of heat.

As explained on p. 851, the rate at which heat passes through a ceramic material either by radiation or conduction is related to its temperature, though this statement must usually be modified on account of the influence of other factors.

The effect of heat on the thermal conductivity of a material may be considered with respect to:

- (i) The heat applied in course of manufacture (i.e. in the burning of ceramic ware).
- (ii) The temperature of the material when in use.

The heat applied during the course of manufacture is very important, as the thermal conductivity usually increases with the temperature of firing. This is often due to the pore spaces being reduced in size and number by being filled with the fused material produced during the burning of the ware at a high temperature. Prolonged burning has a similar effect. The best heat-insulating qualities are obtained, according to A. L. Queneau, by burning the materials at the lowest possible temperature consistent with their satisfactoriness in use.

Table XIV.XV shows the effect of the burning temperature on the thermal conductivity of various refractory materials.

TABLE XIV—XV. EFFECT OF BURNING TEMPERATURE ON
THERMAL CONDUCTIVITY
(after Wologdine)

	<i>Burning Temperature</i>	<i>Gm.-cals.</i>	<i>Kg.-cals.</i>	<i>Porosity per cent</i>
Fireclay bricks	1050	0.0035	1.25	29.4
Fireclaybricks	1200	0.0030	1.07	—
Fireclay bricks	1300	0.0050	1.81	24.1
Fireclay bricks	1300	0.0042	1.50	30.2
Fireclay retorts	1300	0.0038	1.37	27.3
Bauxite bricks	1050	0.0031	1.11	41.5
Bauzite bricks	1300	0.0033	1.19	38.4
Silica bricks	1050	0.0020	0.71	42.5
Silica bricks	1300	0.0031	1.12	42.9
Magnesia bricks	1050	0.0058	2.08	35.1
Magnesia bricks	1300	0.0065	2.35	41.0
Chromite	—	0.0066	2.37	—
Graphite	—	0.0250	9.00	—
Kieselguhr	—	0.0018	0.64	58.0
Hard porcelain	1400	0.0043	1.55	—

The temperature of a ceramic material when in use has also a very important influence on the thermal conductivity. In most cases, the conductivity increases at high temperatures, the extent of the increase depending on the nature of the material. Thus, the thermal conductivity of fireclay and grog bricks increases considerably when they are heated to 1200° C., whereas that of chromite bricks is hardly affected, and that of magnesia bricks decreases slightly at high temperatures. **Clay wares** have a thermal conductivity depending on their texture, those which are vitrified being usually better conductors than those which are more porous. The thermal conductivity of fireclay bricks is almost always less than 0.0050 gram-cals., and is usually about half this figure; the thermal conductivity of building bricks is

similar. Table XIV.XVI, due to L. R. Ingersoll, shows the average diffusivity of fireclay bricks in comparison with other materials, including some metals:

TABLE XIV—XVI. THERMAL CONDUCTIVITY OF VARIOUS MATERIALS

<i>Material</i>	<i>Diffusivity</i>	<i>Material</i>	<i>Diffusivity</i>
Air	0.1800	Gold	1.1800
Building brick	0.0050	Iron	0.1700
Cast steel	0.1200	Silica brick	0.0030
Copper	1.1300	Silver	1.7400
Firebrick	0.0067		

Thermal conductivities of numerous refractory materials using a modified form of the apparatus described on p. 854 are shown in Table XIV.XVII; values were determined at several hot face temperatures.

TABLE XIV—XVII. THERMAL CONDUCTIVITY VALUES

<i>Material</i>	<i>Thermal conductivity (B.T.U's/sq. ft./Hr./1° F.)</i>		
	450° C.	720° C.	940° C.
Firebrick (28% Al_2O_3)	5.8	7.9	9.8
Aluminous brick (72% Al_2O_3)	6.8	9.1	13.4
Sillimanite (kyanite) brick	6.5	8.1	10.9
Silica brick	6.3	8.4	11.2
Magnesite brick	42.3	29.4	18.6
Chrome-magnesite brick	29.6	22.6	15.4
Chrome brick	14.2	13.2	14.0
Diatomite brick	0.8	1.1	—
Porous fireclay brick	1.6	2.3	2.8

Retorts, muffles, and saggars require to have as high a thermal conductivity as possible, so as not to waste fuel in heating them rather than their contents. Complete satisfaction is very difficult to obtain as the highest thermal conductivity is associated with materials which are dense in texture, whereas resistance to the changes in temperature to which such articles are exposed necessitates the use of a porous mass.

The thermal conductivity of **refractory porcelain** is about 0.002–0.004 gm-cal., or rather higher than that of glass.

Lees and Chorlton found the thermal conductivity of a sample of porcelain tested to be 0.00248 between 92° C. and 98° C.

Most refractory materials have somewhat similar thermal conductivity coefficients and these tend to increase at higher temperatures. The notable exception is magnesite and as Table XIV.XVII shows, magnesite and to a lesser extent chrome-magnesite refractories have a much greater coefficient and this *decreases* appreciably with increasing temperature.

Silicon carbide bricks have a high thermal conductivity; even when mixed with as much as 20 per cent of clay they conduct three times as much heat as magnesia bricks, seven times as much as fireclay bricks, and twelve times as much as silica bricks in a given time.

Graphite bricks, according to Heyn, Bauer and Wetzel have a thermal conductivity of about 0.0012 C.G.S. units, about five times that of fireclay bricks.

When bricks or blocks are cemented together to form a wall, as in a furnace, the thermal conductivity may be much altered, and Dougill, Hodsmen and Cobb have pointed out that the thermal conductivity of the joints of brickwork is only one-tenth that of the bricks themselves, so that segmental retorts would appear to require more heat than those in one piece, if both kinds of retorts are made of the same material.

Table XIV.XVIII, due to Harvard, shows the thermal conductivity of various raw ceramic materials in C.G.S. units between 20° C. and 100° C., the materials in each case being in the form of a powder which passed entirely through a sieve with 600-meshes per sq. cm. (approximately 60 meshes per linear inch).

TABLE XIV—XVIII. THERMAL CONDUCTIVITY OF POWDERS

<i>Material</i>	<i>Thermal Conductivity in gm.-cal. sec. per cm.² per 1° C.</i>	<i>Material</i>	<i>Thermal Conductivity in gm.-cal. sec. per cm.² per 1° C.</i>
White Calais sand	0-00060	Lime	0-00029
Fine silicon carbide	0-00050	Fused magnesia	0-00047
Coarse carbide	0-00051	Mabor magnesia brick	0-00050
Enamel quartz	0-00036	Calcined Greek magnesia	0-00045
Fused quartz	0-00039	Calcined Veitsch magnesia	0-00034
Fireclay brick	0-00028	Pattinson's high calcined magnesia	0-00016
Retort graphite	0-00040	Kieselguhr	0-00013

The thermal conductivities of various *electrical ceramic materials* are shown in Table XIV—XIX.

TABLE XIV—XIX. THERMAL CONDUCTIVITIES OF ELECTRICAL CERAMIC BODIES

	<i>Thermal Conductivities</i>	
	<i>gm. cal./cm.²/sec./°C.</i>	<i>B.T.U./sq. ft./hr./°F.</i>
Porcelain	0-002-0-004	5-8-12-0
Steatite	0-005-0-006	15-0-18-0
Cordierite	0-003-0-005	9-0-15-0
Zircon	0-011-0-012	30-0-36-0
Rutile	0-007-0-010	20-0-30-0
Titanate	0-008-0-0095	24-0-30-0

Cermets, or composite metal-ceramic bodies usually have a high thermal conductivity and some have similar values to those of metals.

Non-siliceous materials usually have a high thermal conductivity and Table XIV.XX, due to Kingery¹ shows values for several pure ceramic materials which were either single crystals or were sintered to a mass of low porosity.

TABLE XIV—XX. THERMAL CONDUCTIVITIES OF SOME CERAMIC MATERIALS

Material	Thermal Conductivity (cals. cm. ² /sec./°C.)		
	100° C.	400° C.	1000° C.
Al ₂ O ₃	0.072	0.031	0.015
BeO	0.525	0.222	0.049
Graphite	0.426	0.268	0.149
MgO	0.086	0.039	0.017
Spinel	0.036	0.024	0.014
ThO ₂	0.025	0.014	0.008
Zircon	(0.016)	0.012	0.010
TiC	0.060	0.032	0.014
TiC cermet	0.083	(0.04)	(0.02)
Mullite	0.015	0.011	0.010
Zirconia	0.0047	0.0049	0.0055

Bracketed figures are estimated values.

Thermal conductivity measurements are particularly liable to variations and are subject to numerous errors. There are many discrepancies between the results reported by different authors and it is not easy to establish absolute values. Ideally the specimen to be tested should be in the form of a sphere or cylinder, but this is not always either convenient or satisfactory. The results obtained by any one worker on a series of materials are comparative within themselves but should not be used in conjunction with other figures obtained under different experimental conditions.

The influence of porosity on the thermal conductivity of various bodies has been studied by Austin.² Fig. XIV.5 indicates the degree of variation which he obtained in specially compacted bodies.

THE INSULATION OF HEAT OR THE THERMAL RESISTIVITY

THE converse of the transmission of heat is termed *insulation* and substances which prevent the transmission of heat or have a very low thermal conductivity are known as *insulators*. They are particularly used for retaining heat in kilns, furnaces, and other heating appliances.

The loss of heat by radiation and convection from a boiler plant frequently reaches 10 per cent of the fuel used; in gas-retorts it is usually nearer 20 per cent, and, with other types of plant, such as metal-heating furnaces and pottery kilns, as much as 60–70 per cent of the heat supplied may be lost. In storage tanks, drying

¹ Kingery, W. D., *J. Amer. Ceram. Soc.*, 38, 3, 1955.

² Austin, J. B., *J. Amer. Ceram. Soc.*, 35, 10, 1952.

chambers, and refrigerating plants, the loss is less noticeable, but is equally important.

The materials available for heat insulation are all characterised by a relatively high proportion of air space, but the smallness of the pores and their lack of communication with each other are even more important than their total volume. If the pores are large and communicate freely with one another, heat may be transmitted by convection across them, even at comparatively low temperatures.

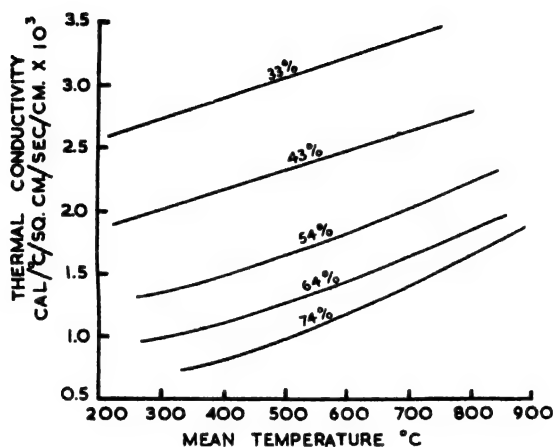


FIG. XIV.5. THE EFFECT OF POROSITY ON THE THERMAL CONDUCTIVITY OF SILICA BRICKS (after Austin)

Heat is also transmitted across the pores by radiation and, as the temperature rises, the quantity radiated increases with great rapidity, until, at 1500° C. it almost equals that conducted through the solid substance, and the material ceases to act as an insulator.

At relatively low temperatures, wood, cork, rubber, rope, mill-board, foamed plastic and various textile materials, are good insulators. For rather higher temperatures aluminium-foil, asbestos, vermiculite, magnesia, porous concrete, slag wool, and glass-silk are suitable, but for still higher temperatures a ceramic material must be used. No insulator is equally suitable for all temperatures.

The insulating power of a material is ascertained by determining the thermal conductivity and then calculating its reciprocal, or by comparing the loss of heat when various insulators are used.

In selecting an insulating material for use at high temperatures it is important to choose only those which are sufficiently refractory, have a low shrinkage when heated to the temperature at which they will be used, and have sufficient strength to support any load or pressure likely to be applied to them.

Table XIV.XXI shows the thermal resistivity of various materials.

Air, when motionless, is often regarded as a heat-insulating material, but

Mellor¹ has shown that for a given size of pore-space, or volume of air, there is a temperature at which the quantity of heat passing through it by radiation equals that which would be carried by a solid substance occupying the same space. For an air-distance of 0.5 cm. the temperature is 730° C.; for 0.1 cm., 1400° C., and for 0.01 cm. the temperature is 3000° C. Hence, the smaller the pore-space the greater is its insulating power.

TABLE XIV—XXI. THERMAL RESISTIVITY

Material	Thermal Ohms	
	in. cube	cm. cube
Silver, 0°–100° C.	0.094	0.24
Platinum, 18°–100° C.	0.55	1.4
Acheson graphite, 100°–390° C.	0.28	0.71
Acheson graphite, 100°–914° C.	0.32	0.82
Electrode carbon, 100°–360° C.	0.50	2.7
Electrode carbon, 100°–942° C.	0.72	1.9
Plumbago brick,	3.8	9.6
Silicon carbide brick	4.1	10.3
Quartz	5.9	15.0
Retort carbon, 0° C.	9.1	23.0
Magnesia brick	13.0	34.0
Chromite brick	16.0	42.0
Firebrick	22.0	57.0
Chequer brick	24.0	61.0
Gas retort brick	25.0	63.0
Building brick	29.0	72.0
Glass pot	35.0	89.0
Porcelain, 95° C.	38.0	96.0
Firestone	39.0	99.0
Terra-cotta	41.0	104.0
Silica brick	47.0	120.0
Kieselguhr brick	52.0	133.0
Plumbago	96.0	240.0
Fine sand	109.0	276.0
Coarse sand	110.0	280.0
Pumice	219.0	558.0
Asbestos	139.0	353.0
Kieselguhr	435.0	1110.0
Kieselguhr	472.0	1200.0
Magnesia, calcined	160.0	407.0
Magnesia calcined	544.0	1380.0
Magnesia calcined	544.0	1410.0

The most important ceramic materials used for heat-insulation are:

(a) *Powdered and Fibrous Materials*, such as slag-wool, glass-silk, asbestos, magnesia, diatomite, or kieselguhr. Most of these are suitable only for use at temperatures below 800° C.

(b) *Diatomite*, kieselguhr, and the like made into bricks or other articles. They have a low crushing strength (seldom exceeding 300 lb. per sq. in.), a low refractoriness, and cannot be used above 800–850° C.

¹ *J. Soc. Chem. Ind.*, 38, 140, R., 1919.

(c) *Vermiculite* which is a hydrated magnesium silicate capable of exfoliation on heating (see p. 157). The material has a high degree of insulating power and can withstand a higher temperature than diatomite.

(d) *Refractory materials* composed of fireclay mixed with paper-pulp, saw-dust or other combustible material which burn away, leaving a highly porous mass the insulating power of which is lower than that of diatomite, but the bricks can resist a much higher temperature.

THERMAL SHOCK RESISTANCE

MANY ceramic materials are unable to withstand sudden changes in temperature without flaking, dunting, spalling, cracking or other form of disintegration. The ability of a substance to resist such treatment is known as its *thermal shock resistance*. Failure of the brick as a result of its inability to withstand sudden temperature changes is manifested in a characteristic corner fracture, cracking or spalling.

Thermal shock is a direct consequence of internal stresses set up in the brick or shape on the application of heat or on too rapid cooling. Most ceramic bodies are poor conductors of heat and, in consequence, unless careful control of the rate of temperature rise is maintained, thermal gradients may be set up between adjacent areas. If the body expands appreciably on heating, some parts of it will increase in volume to a greater extent than others due to the differences in temperature; stresses will arise which, if they exceed the elastic limit of the body, will cause spalling.

The principal factors which contribute to a low thermal shock resistance are:

- (a) A high coefficient of thermal expansion.
- (b) A low thermal conductivity or diffusivity.
- (c) An inability to accommodate stresses, or in other words, a high modulus of elasticity.
- (d) A low tensile strength.

Although thermal spalling and some of the factors which contribute to it have been studied for many years, the inter-relation of the various properties of an article with its thermal shock resistance have been elucidated only recently, and even now, except for some pure oxides, the conclusions are only empirical.

Kingery¹ has shown that an important factor which influences the thermal shock resistance of a material is its surface heat-transfer coefficient, i.e. its ability to absorb or give up heat to the surrounding medium.

If the surface heat-transfer coefficient is large, i.e. if heat is exchanged readily, the thermal shock resistance (R) can be expressed as:

$$R = S_t(1 - \mu)/E\alpha \quad . \quad . \quad . \quad (a)$$

but, if the heat transfer coefficient is low, the thermal shock resistance (R') is more correctly represented by the equation:

$$R' = kS_t(1 - \mu)/E\alpha \quad . \quad . \quad . \quad (b)$$

¹ Kingery, W. D., *J. Amer. Ceram. Soc.*, 38, 3, 1955.

where S_t = the tensile strength of the material at the temperature of the test (t).

μ = Poisson's ratio (see p. 798).

E = the coefficient of elasticity.

α = the thermal expansion.

k = the thermal conductivity.

For most ceramic materials, Poisson's ratio is reasonably constant (p. 798) and does not change much with temperature and although the strength of a body can vary between wide limits, the elasticity coefficient E changes similarly, so that the ratio S_t/E is not very different for many materials. At high temperatures, however, the strength may be drastically reduced and this tends to increase the thermal shock tendency, but when liquid forms, there is a considerable increase in elasticity, so that spalling resistance increases.

The thermal conductivity and expansion have a considerable effect on the thermal shock resistance and the ratio of these two values is often an indication of the spalling tendency of a material.

Kingery has derived thermal stress resistance factors for some ceramic materials and these are shown in Table XIV.XXII.

TABLE XIV—XXII. THERMAL STRESS RESISTANCE FACTORS
FOR SOME CERAMIC MATERIALS
(after Kingery)

Material	100° C.		400° C.		1000° C.	
	<i>R</i>	<i>R'</i>	<i>R</i>	<i>R'</i>	<i>R</i>	<i>R'</i>
Al ₂ O ₃	37	2.7	36	1.1	40	0.6
BeO	33	17.3	31	6.9	14	0.7
MgO	22	1.9	24	0.9	26	0.5
Mullite	75	1.1	68	0.8	84	0.8
Spinel	32	1.2	32	0.8	32	0.5
ThO ₂	51	1.3	47	0.7	37	0.3
Zircon	137	(2.2)	115	1.4	73	0.7
ZrO ₂	66	0.3	62	0.3	53	0.3
Fused silica	2500	9.5	2400	10.1	—	—
Glass (soda-lime-silica)	94	0.4	94	0.4	—	—
TiC	42	2.5	40	1.3	(40)	0.6
Porcelain	116	0.5	103	0.4	116	0.5
Fireclay	38	0.1	41	0.1	178	0.5
TiC cermet	208	(17.3)	200	(8)	198	(4)

Bracketed figures are estimated values.

Before the thermal shock behaviour of a material can be assessed, the surface heat-transfer coefficient must be determined. This is not an easy matter because so many factors can have an important influence; these include (i) the size and shape of the body; (ii) its surface texture; (iii) the nature of the surrounding medium. Bodies quenched in air or subjected to the impingement of hot gases on their surface, generally have a much lower surface heat transfer than when the quenching or heating medium is a liquid.

The reversible thermal expansion frequently determines the tendency of a ceramic material to spall. When the expansion coefficient is high, as in silica and siliceous materials, the rate of heating should be slow so as to reduce the temperature gradients to a minimum. Silica minerals, however, have a high expansion coefficient only at comparatively low temperatures as a result of the inversions (see p. 722). Once this critical temperature has been exceeded only a negligible increase in volume occurs and the tendency to thermal shock is considerably reduced.

Materials with a high thermal diffusivity have little tendency to spalling even though the coefficient of expansion may be appreciable. Such materials are not common in ceramic studies although magnesia provides an interesting case. As will be seen in Table XII.IX (p. 722), bricks made of this material have a comparatively large thermal expansion, but because the conductivity is also high at low temperatures (see Table XIV.XVII, p. 860), they have a moderately good resistance to thermal shock. At higher temperatures, however, the expansion is maintained but the conductivity is markedly decreased; hence, the tendency to spall becomes a serious factor.

The ability to accommodate stresses which may be set up from thermal gradients in a body is not easy to measure. A vitrified mass is more liable to spall than one where crystalline development predominates, but probably the greatest factor is the porosity of the body.

There are many anomalies in the literature on the subject of the effect of porosity on the spalling tendency of the body. When a high porosity is induced in a ceramic body by underfiring, the composition may also be quite different so that a direct comparison is valueless. Furthermore, a spalling crack in a porous body may be less obvious than one in a dense article, so unless careful measurements are made, a misleading conclusion may be reached.

A porous refractory block usually shows less tendency to disintegrate under rapid heating and cooling conditions than does a dense brick, but measurements of the elasticity coefficient by sonic methods have shown that spalling occurs readily in porous shapes, but the cracks which result are not continuous and frequently do not involve a loss of material, but they do involve a loss of strength.

Coble and Kingery¹ have studied the influence of porosity on the thermal shock resistance of sintered alumina and conclude that the spalling tendency is *increased* by a factor between three and six times for an increase in porosity of 50 per cent.

Eusner and Debenham² concluded that small increases in porosity in a dense fireclay brick cause a *reduction* in the thermal shock resistance, but that there was no direct correlation between the two properties if the porosity was above 10 per cent. They found that the method of forming the bricks contributed to the spalling tendency; induced laminations were frequent sources of spalling cracks.

The tendency to spall may be measured in several ways. The Institution of Gas Engineers³ specifies that test pieces measuring 2 in. \times 2 in. \times 3 in. should be placed in a furnace maintained at a constant temperature for 10 minutes and then withdrawn and placed on a cool floor for the same period of time. The cycle of heating

¹ Coble, R. L. and Kingery, W. D., *J. Amer. Ceram. Soc.*, 38, 33, 1955.

² Eusner, G. R. and Debenham, W. S., *Bull. Amer. Ceram. Soc.*, 31, 489, 1952.

³ *British Standard*, No. 1902, 1952.

and cooling should be repeated until spalling occurs. After each cycle the specimen should be examined for incipient cracks or fractures. The thermal shock resistance is expressed in terms of the number of cycles required to cause a 50 per cent loss in the volume of the test pieces. The temperature recommended for carrying out the test is 450° C. for silica and siliceous materials and 950° C. for all others.

The American Society for Testing Materials¹ prefers the panel spalling method in which nine or more bricks are built into a furnace door. Once the required temperature has been reached the door is closed and the test panel is exposed to the hot atmosphere, usually for 10 minutes, after which it is withdrawn and cooled with an air-water blast for a further 10 minutes. The cycle is repeated twelve times and the loss in weight of the panel recorded.

The most positive method of measuring the thermal shock tendency of materials is to establish the temperature difference between the surroundings and the body which is just sufficient to cause spalling. The maximum stresses which the body can withstand are thus established and the results on different materials are directly comparable. The simplest method using this principle is to quench a cylinder or block of material from a controlled furnace temperature into air, water or other suitable medium. The temperature of the specimen prior to quenching can be raised by small increments until the critical temperature difference to cause spalling is reached.

Buessem and Bush² have devised a method for measuring thermal shock resistance in which a pile of rings of the material under test are heated from the inside by an electric element and cooled on the outside. The temperature gradient across the rings can be raised gradually until spalling occurs.

The resistance of *fireclay* bricks and other clay products to thermal shock depends largely on the proportion of quartz or free silica in them. Grog bricks are less likely to crack than fireclay bricks made wholly of clays, and aluminous bricks—in which most of the clay has been converted into crystalline mullite—are still more resistant to sudden changes in temperature. Fireclay bricks of good quality and reasonably porous should not lose more than 12 per cent by weight when subjected to the spalling test described above, but bricks having a very close texture may lose up to 65 per cent by weight.

Large blocks are more susceptible to sudden changes in temperature than are smaller ones, but if properly made they should resist all ordinary conditions of heating and cooling. To secure the necessary resistance they should have a more open texture than is needed for bricks or small blocks, so that the pores may take up any strains which occur.

Saggars made of fireclay must be reasonably constant in volume when in use or they may warp and lose their shape. This will cause them to fit badly on one another and possibly endanger the stability of the 'bungs' of saggars placed one above another in the kiln. Saggars should be as porous as is consistent with the necessary strength.

Glass-melting pots and retorts require to be very resistant to sudden changes in temperature, but it is difficult to secure this property at the same time as a high

¹ *A.S.T.M.*, Designation C38-49.

² Buessem, W. R. and Bush, E. A., *J. Amer. Ceram. Soc.*, 38, 27, 1955.

resistance to corrosion. Moderately porous materials are the most suitable for the purpose where the corrosion is not excessive.

Crucibles must be very resistant to sudden changes of temperature, as when in use they are withdrawn rapidly—from a furnace (which may have a temperature up to 1800° C.) into the open air. This resistance is attained if the crucible has an open, porous texture which may be obtained in the case of fireclay crucibles by introducing a sufficiently large proportion of grog into the mixture of which the crucibles are made. The number of times which a crucible can be reheated varies according to its contents and the manner in which it is used.

Silica bricks are very susceptible to sudden changes in temperature and soon develop fine cracks, which later increase in size and cause the bricks to become weak or to spall and flake. Most silica bricks are so sensitive to changes in temperature, that if a current of air is drawn through them during the cooling of the kiln they are liable to crack. For this reason, after the firing of the bricks is completed, the kilns are closed and allowed to cool in such a manner that the whole of the heat is lost by radiation through the walls and floor of the kiln.

The great liability of silica bricks spalling at temperatures below 500° C. is due to the α - β transition range described on p. 722.

Silica bricks are only liable to spall at low temperatures (see p. 867) and at high temperatures are extremely resistant to thermal shock. A good quality product may be used quite safely in the roof of a basic open hearth furnace where, on the reversal of the firing cycle, the temperature may fluctuate between 1650° C. and 1200° C. in a matter of seconds. The crystal type of silica present governs the safe lower limit of temperature. If quartz is present, spalling is always liable below 573° C.; when cristobalite is the principal modification present, the brick is 'safe' above about 300° C.; tridymite bricks can be used with comparative safety at temperatures above 170° C. Under normal testing conditions as described on p. 867, however, silica bricks rarely withstand more than one cycle.

Bauxite bricks are liable to crack when exposed to sudden changes of temperature unless they have been made of very well-burned material. Bricks made of fused alumina are much more resistant to sudden changes in temperature than bricks made of calcined bauxite, the best results being obtained when the alumina is in large crystals.

Magnesite bricks are particularly subject to spalling but only at high temperatures. The reasons for this unusual behaviour have been outlined on p. 867.

Zirconia and **zircon** refractories are very resistant to temperature changes and for this reason, their use may increase in the near future.

Chromite bricks, according to Hartmann and Hougen, are very susceptible to sudden changes of temperature, and are wholly disintegrated by the spalling test described on p. 867.

Carbon bricks are quite insensitive to sudden changes of temperature as their coefficient of expansion is very low.

Silicon carbide bricks are also very insensitive, especially those made from carbofrax, which Hartmann and Hougen¹ found to lose only 0.3–8 per cent of their weight when subjected to the very stringent test described on p. 867.

¹ *Brick and Clay Record*, 56, 934, 1920.

Crazing, peeling and allied phenomena are specialised types of thermal shock. If the glaze and body compositions are not correctly adjusted so that the coefficients of expansion are closely similar, one will increase in length at a greater rate than the other when heated. If the elastic limit of the glaze is exceeded as a consequence, then it will fracture. In many cases it is impossible to adjust the expansion of the glaze to that of the body without losing other desirable characteristics. Engobes are therefore used, which act as a bridge between the expansion of the body and glaze; these are materials which have intermediate expansion coefficients and so lessen the possibilities of cracking (see p. 341).

With the advent of jet and rocket propulsion and atomic energy, an urgent need has arisen for materials capable of resisting high temperatures and very rapid heating rates. All refractory bodies so far developed disintegrate rapidly under these conditions because of their comparatively low resistance to thermal shock, and the metals which are available melt under the conditions of operation. For these reasons, attempts have been made to 'wed' metals and ceramics in the hopes that such a 'marriage' would produce a substance with the high elasticity coefficient of the former and the high softening point of the latter. Such developments are outside the scope of this volume, but it is likely that *cermets* (as the metal-ceramic products have been named) will, within the next few years, open up a new era of high temperature operations.

ELECTRICAL PROPERTIES

THE electrical properties of ceramic materials are important in connection with both their manufacture and use. These properties include:

(1) The capacity of clays when suspended in water to conduct an electric current. The nature of the colloidal minerals in clays and their ionisation tendency (p. 433) determines their conductivity to a very large extent. When subjected to a direct current, the solid particles in a clay suspension migrate towards the positive electrode. This property, known as *electro-osmosis* and *kataphoresis* is occasionally used in the purification of clays and as a means of dewatering them.

(2) The high electrical resistance possessed by many ceramic materials. For this reason, porcelains are commonly employed as resistors and insulators in electrical installations.

(3) Their dielectric capacity. Ceramic materials are widely employed as the dielectric medium in condensers and as cores in transformers.

Clay Slips possess electrical properties which are often important in connection with the purification of these materials and in the production of ware by the casting process. Thus, whilst the electrical conductivity of pure, distilled water is 10^{-6} reciprocal ohms (or *mhos*) at 18° C., the presence of even minute quantities of soluble salts causes large differences in the conductivity. When larger proportions are present, the conductivity does not conform to simple rules, but is dependent on several complex considerations.

The conductivity of solutions at different temperatures varies considerably; it may be calculated from the formula:

$$C_t = C_{18}(1 + k(t + 18))$$

where C_t is the conductivity at any given temperature t in $^{\circ}\text{C}$., C_{18} is the conductivity at 18°C ., and k is the temperature coefficient. For salts, the temperature coefficient varies from 0.02–0.023; for acids, and for some acid salts it is 0.009–0.016; and for caustic alkalies about 0.02 ohms per c.c.

The electrical conductivity of clay slips depends chiefly on the proportion of soluble salts present in the water but also on the type of clay. Thus, Bleininger and Kinnison¹ found the results shown in Table XIV.XXIII.

TABLE XIV—XXIII. ELECTRICAL RESISTIVITY OF SLIPS

	<i>Soluble Salts per cent</i>	<i>Resistance in ohms reduced to 60° F.</i>
Surface clay, Cleveland	2.10	2110
Surface clay, Curtice	1.50	2160
No. 3 Fireclay, Aultman	0.94	3790
Shale, Canton	0.77	3050
Shale, Independence	0.60	3970

The presence of calcium sulphate in solution in clay slips greatly decreases their electrical resistivity. In one case, examined by Bleininger and Kinnison, the presence of 0.072 per cent in a kaolin slip decreased the resistance from 4440 to 720 ohms per c.c.

ELECTRICAL CONDUCTIVITY AND RESISTIVITY OF CERAMIC MATERIALS

THE conduction of electricity in materials is the result of ionic or electronic movement throughout the mass of the body. In solutions and some melts, the freedom of movement of the individual ions is the determining factor, but in solid materials this is, for the most part non-existent, and conductivity depends on the ease with which electrons can move about the body. Some materials, such as the metals, have so-called *free electrons* which can wander, almost without restriction, between the electronic orbitals of the ions; these electrons facilitate the passage of electricity and impart a high conductivity to the mass. Most other solid materials do not contain a high proportion of such 'free electrons' but nevertheless defects within the structure of crystals may permit some electron movement and a consequent conduction of electricity.

When cold, most ceramic materials are practically non-conductors, but, owing to the resistance they offer to the current, they become heated in time and the conductivity rises rapidly with the temperature up to about 1000°C . and then remains almost constant. When in a molten state, most silicates behave as electrolytes and as dissociated substances in solution. Bleininger² has suggested that the softening point of the principal constituent (eutectic) can be determined by the change in the conductivity at the point of fusion.

The electrical conductivity and resistivity of ceramic materials are expressed in different ways according to convenience:

¹ *Trans. Amer. Ceram. Soc.*, 15, 523, 1913.

² *Amer. J. Sci.*, 44, 242, 1892.

1. The *electrical conductivity* may be expressed directly in C.G.S. units as *mho* (or reciprocal ohms) per centimetre.

2. The *electrical resistance* may also be expressed in C.G.S. units as *ohms* per centimetre (the temperature being also stated both in this and the electrical conductivity).

The electrical resistivity of insulators at high temperatures may be calculated from the formula $E \times k$, where E is the observed resistance and k is a constant depending on the shape of the insulator. In cup-shaped insulators,

$$k = \frac{\pi d^2}{4t}$$

where d is the diameter of the bottom and t the thickness of the cup. In the case of tubular insulators,

$$k = \frac{2\pi l}{2.30 \log_{10} \frac{R_2}{R_1}}$$

where l is the length of the external conducting band and R_2 and R_1 are respectively the external and internal radii of the insulator.

3. The *breakdown* or *puncture voltage*, is the voltage at which a piece of the material of definite thickness is unable to act as an insulator, and, therefore, allows the electric current to pass through it. According to H. F. Howarth, there is no direct relation between the specific ohmic resistance and the puncture voltage.

4. The *arc-over voltage* is that at which an electric current 'jumps the gap' between an insulator and an electrode and depends on the distance between them, as well as on the resistance of the insulator. The minimum permissible distance (in inches) is usually taken to be numerically equal to the voltage divided by 3000.

British Standard Specification No. 116 specifies the arc-over voltage as at least 10 per cent more than the *one-minute* test, which consists in exposing the insulator for one minute to a voltage equal to $(2\frac{1}{2} V + 2000)$ where V is the line-voltage.

5. The *di-electric* or *electric strength* is another term used to indicate puncture voltage. It is expressed by the number of volts per mm. of thickness of the insulator which must be passed at 250° C. before a current will flow. For pieces 0.25 in. thick, the electric strength of a porcelain insulator should be at least 200 volts per mm. The di-electric strength diminishes rapidly as the temperature increases.

The force (f) of repulsion between two point charges (e, e^1) of electricity at a distance (r) apart in a uniform medium of great extent is:

$$f = ee^1/\epsilon r^2;$$

ϵ depends on the nature of the medium and is termed the *dielectric constant*.

6. The '*Te*' value or the temperature at which the electrical resistance is reduced to 1 megohm per cm.

7. The *specific inductive capacity* or the relative dielectric strength of the article or material, that of an equal thickness of air being taken as unity.

The general factors influencing the electrical conductivity and resistivity of ceramic materials are:

1. The composition of the material.
2. The size of the article or test piece at the time.
3. The density and texture of the material.
4. The manner of heating and the extent to which the material has been heated during the 'burning' of the ware.
5. The piezo-electric effect.
6. The temperature of the ware.
7. The length of exposure to the electric current.

The electric current can take two paths through a ceramic material (i) directly through a mass as a whole—*volume conductivity*. It is measured by placing two equal-sized conductor plates at opposite ends of the material so as to form a circuit and passing the current through it. (ii) Chiefly (or wholly) through the surface layers—*surface conductivity*. It varies with the humidity of the atmosphere and is probably due, in many cases, to the condensation or absorption of oil or moisture; the latter may, in time, dissolve small quantities of electrolytes (alkalies, soluble salts, etc.) from the material and so produce a conducting film.

Some materials are used as *conductors* but others, including some ceramic articles, are used to resist or wholly prevent the passage of an electric current, i.e. as *insulators*. Thus resistance may be regarded as the opposite of conductivity and expressed as the *reciprocal* of conductivity. Thus if the conductivity is represented by the letter ϵ , the resistance or resistivity (τ) would be represented by the expression $1/\epsilon$ so that

$$\tau = \frac{1}{\epsilon}$$

When considering conductors it is simple to refer to their conductivity; when insulators are under consideration it is often better to refer to their resistance or resistivity.

The *composition* of the ceramic material largely determines its electrical properties, some materials being much better conductors than others. In composite materials, such as porcelain, the chemical composition is usually important only in so far as it modifies the structure, compositions giving a dense vitreous mass being usually better insulators than those which produce semi-vitreous or porous wares.

Table XIV.XXIV shows the electrical conductivity of various materials used in the ceramic industries or liable to occur as impurities in ceramic materials.

Fig. XIV.6 shows the variation with temperature of the resistivity of some electrical ceramic materials; steatite and zircon bodies have exceptionally high values and these are maintained up to high temperatures. Electrical porcelains made of clay, feldspar and flint, have a high resistivity at room temperature, but it falls rapidly with increasing temperature, and the T_e value is between 300°–500° C.

The T_e value can be increased by replacing feldspar with other fluxes which do not contain alkali. The presence of sodium and potassium in a porcelain body reduces the resistivity especially at high temperatures.

The *size of the article* is often important with respect to its insulating power; the resistivity is directly proportional to the thickness.

The *density and texture* of a ceramic material influence the electrical resistivity to a marked degree. The greatest resistivity is found in bodies with low porosity.

The *heat treatment* of the ware affects the resistivity; hard firing tends to increase its value but over-firing, especially if blobs or flaws are produced, causes a reduction. The *Te* value of porcelain is affected by the rate of cooling; rapid cooling produces a closer and more vitreous structure than slow cooling.

TABLE XIV—XXIV. ELECTRICAL CONDUCTIVITY OF VARIOUS MINERALS

<i>Good Conductors</i>	<i>Moderate Conductors</i>	<i>Bad Conductors</i>	
Magnetite	Ferriferous amphiboles and pyroxenes	Siderite	Apatite
Titaniferous magnetite		Xenotime	Andalusite
Magnetic haematite	Biotite	Epidote	Sillimanite
Pyrrhotite	Tourmaline	Olivine	Diamond
Chromite	Titanite	Staurolite	Topaz
Ilmenite	Rutile	Garnet	Spinel
Haematite	Anatase	Monazite	Kyanite
Wolframite	Brookite	Gypsum	Corundum
Spinel	Cassiterite	Quartz	Celestite
Ferriferous cassiterite		Chalcedony	Zircon
Tantalite		Felspars	Sandstone
Iron pyrite		Calcite	Granite
Chalcopyrite		Dolomite	Porphyry
		Cordierite	Schist
		Barytes	Fluorspar
		Phlogopite	Silicates
		Muscovite	Clays
		Tremolite	

The *piezo-electric effect*, in which an electric current is produced by pressure, sometimes seriously reduces the electrical resistance of an insulator if the latter is under compression. Some specimens of quartz and porcelain exhibit this phenomenon, especially in the case of quartz crystals, when the pressure is applied to two diametrically opposite faces parallel to the major axes; a potential difference is then set up in the faces perpendicular to those in which the pressure is applied, this difference varying directly as the pressure. The converse of this may also occur when some quartz crystals are subjected to the prolonged action of an electric current and a change in the dimensions of the crystals may then result, an expansion occurring along one axis and a contraction along another. If these changes are hampered by the surrounding magma, great local stresses may occur; consequently, when a piece of porcelain is placed in an alternating field of electrostatic force, a vibratory movement results, owing to the repeated changes in the dimensions of quartz or other crystals similarly affected, and these vibrations may cause a rupture along the cleavage planes of the crystals and also between the crystals and the matrix. The rupture may result in a leakage of current through the spaces so formed, and the dielectric strength then rapidly deteriorates. The piezo-electric effect appears to be exhibited only in connection with certain crystals; it is, therefore, at a minimum in those porcelains in which the quartz crystals originally present in the raw materials have been most completely dissolved in the felspathic ground mass by prolonged

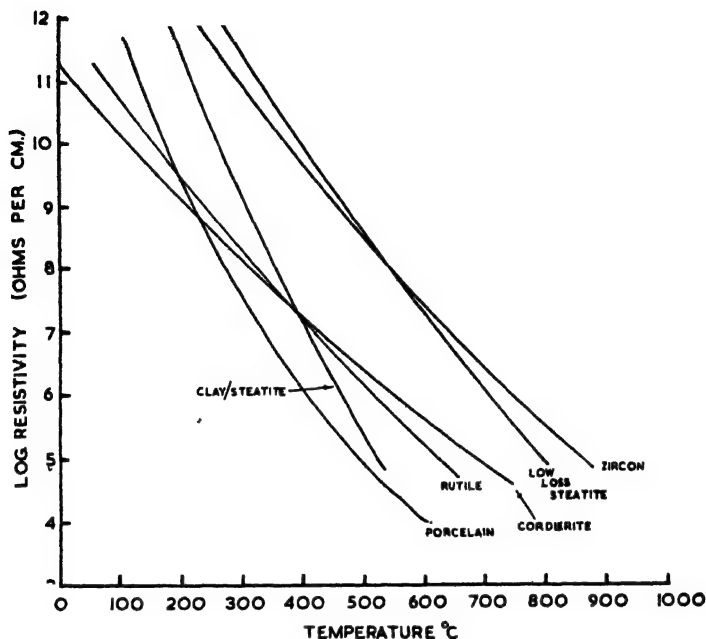


FIG. XIV.6. THE VARIATION OF THE RESISTIVITY OF SOME ELECTRICAL CERAMIC MATERIALS WITH TEMPERATURE

heating at a suitable temperature. So far as can be ascertained, mullite crystals—which are also formed in most well-burned porcelains—do not show this effect.

The *temperature of the ware* when in use has a notable effect on the electrical resistance or insulating power, as most ceramic materials become much better conductors of electricity when at a high temperature than when cold. This is well shown in Fig. XIV.6.

The *duration of exposure to an electric current* has a noteworthy effect on the apparent resistivity or dielectric strength of porcelains, as a much lower voltage applied for a long time will puncture the material in the same manner as a current of high voltage applied only for a very short time. In making comparative tests it is, therefore, important to state the time during which the current was applied.

The *electric sensitiveness* of insulators is tested by heating the sample in water to 50° C. for one hour, then placing it in ice-water for an hour, and, after wiping it dry, subjecting it three times in succession to a flash-voltage.

Clays. The electrical resistivity of raw clay is usually regarded as fairly constant, but that of burned clay varies considerably according to the extent of the burning, the changes which have taken place during that process, and the temperature of testing. Thus, according to Hartmann, Sullivan and Allen,¹ the resistivity of fire-clay bricks at different temperatures is as follows:

¹ *J. Amer. Electrochem. Soc.*, 38, 279, 1920.

TABLE XIV—XXV. ELECTRICAL RESISTIVITY OF FIRECLAY BRICKS

<i>Temperature</i>	<i>Electrical Resistivity</i>	<i>Temperature</i>	<i>Electrical Resistivity</i>
° C.	<i>ohms per cc.</i>	° C.	<i>ohms per cc.</i>
Cold	Less than 137,000,000	1200	Less than 4,160
800	57,600	1300	2,460
900	20,600	1400	1,420
1000	10,800	1500	890
1100	6,590		

Porcelain. The electrical insulating power of porcelain and stoneware depends largely on the texture and density, and these are controlled by the chemical composition and the manner of burning. Porcelains high in quartz have a low resistance, because of the piezo-electric effect described on p. 874; when the quartz is replaced by mullite or clay, the dielectric strength increases. Porcelains high in quartz also tend to be more porous than those richer in fluxes, and, consequently, have a lower dielectric strength.

According to Bleininger and Riddle,¹ the replacement of quartz by kaolin increases the 'Te' value of a porcelain, but the use of ball clay reduces the electrical resistance. Fused alumina notably increases the 'Te' value, as also does artificial mullite, provided it is not in large crystals.

According to B. S. Radcliffe,² high-grade fireclays mixed with felspar produce materials with as high a dielectric strength as potash porcelains vitrifying at the same temperature. Ceramic wares in which lime is used as flux instead of potash felspar have, according to B. S. Radcliffe, a lower dielectric strength. Thus, a body containing 6-8 per cent of lime having the same porosity, burned at about the same temperature as a felspar porcelain, was found to have only about half the dielectric strength of the latter. B. S. Radcliffe also found that porcelains made with soda-felspar have a greater dielectric strength than those made with potash felspar, though Minneman considers the difference to be too slight to be of importance, provided the porcelain is well vitrified.

The proportion of flux in a porcelain also affects its electrical resistance. Thus, when the felspar content is high the dielectric strength varies directly with the proportion of felspar present, but when the felspar is low the dielectric strength varies directly with the clay content. It also varies inversely with increases of flint or china clay and increases rapidly with the maximum temperature attained in firing. These investigators found that the greatest dielectric strength is obtained with a porcelain containing a high percentage of felspar and a low percentage of flint, whilst the lowest strength in a porcelain is with a low percentage of felspar and a high percentage of flint.

Weimer and Dun³ found that (i) at high temperatures porcelains high in felspar have a lower dielectric strength than those which have less felspar, probably on account of the former softening more readily; (ii) the addition of clay at the expense

¹ *J. Amer. Ceram. Soc.* 2, 564, 1919

² *Trans. Amer. Ceram. Soc.*, 14, 575, 1912.

³ *Trans. Amer. Ceram. Soc.*, 14, 280, 1912.

of flint increases the dielectric strength. Purdy and Potts,¹ however, consider the highest dielectric strength is obtained with a porcelain containing 25–35 per cent of felspar and not less than 40 per cent of clay.

The following figures may be regarded as typical of the porcelains investigated, but porcelains vary so greatly that no figures of general application can be given.

The puncture voltage of porcelain at 25° C. is, according to G. Weimer and C. T. Dun, 64,500–67,500 volts for a thickness of 0.15 inch. It is not generally less than 70,000 volts for pieces $\frac{1}{4}$ in. thick and 100,000 volts for pieces $\frac{1}{2}$ in. thick. E. Rosenthal has stated that the puncture voltage of Berlin porcelain 0.1 in. thick is 40,000 volts. The dielectric constant of Berlin porcelain, according to H. Starke, is 5.73 megohms per c.c. That of Seger porcelain is 6.61 and that of statuary porcelain (Parian ware) is 6.84 megohms per c.c.

TABLE XIV—XXVI. THE ELECTRICAL CONDUCTIVITY OF BERLIN PORCELAIN AT DIFFERENT TEMPERATURES

Temperature ° C.	Electrical Conductivity	Temperature ° C.	Electrical Conductivity
50	0.465×10^{-15}	600	0.6×10^{-8}
70	0.25×10^{-13}	727	0.62×10^{-8}
160	0.582×10^{-12}	800	0.55×10^{-8}
189	0.26×10^{-11}	1000	1.0×10^{-8}
400	0.50×10^{-8}	1100	1.3×10^{-8}

TABLE XIV—XXVII. THE PUNCTURE VOLTAGE OF PORCELAIN AT TEMPERATURES UP TO 300° C.

(G. Weimer and C. T. Dun)

(The test pieces were 0.15 in. thick)

Temperature ° C.	Puncture Voltage	Temperature ° C.	Puncture Voltage
25	64,500–67,500	175	39,000–41,000
50	64,250–67,000	200	26,500–29,500
75	63,000–66,500	225	15,000–22,000
100	62,000–63,500	250	7,500–15,000
125	57,000–60,000	275	4,500–11,500
150	49,500–52,500	300	3,000–7,000

If the porcelain is heated, its dielectric strength—like that of quartz, mica, hornblende, quartz-glass, and ordinary glass—decreases rapidly as the temperature rises. With a rise in temperature of only 100° C. the reduction in the dielectric strength is considerable, and with a rise of 300° C. porcelain becomes only a very poor insulator. This is still further shown in Tables XIV.XXVI, XIV.XXVII and XIV.XXVIII.

¹ *Trans. Amer. Ceram. Soc.*, 13, 431, 1911.

TABLE XIV—XXVIII. 'Te' VALUE OF CERAMIC INSULATORS
(F. B. Silsbee and R. K. Honaman*)

Material	'Te' Value ° C.	Material	'Te' Value ° C.
Fused silica	890	Aviation porcelain	650
Best porcelain	790	Automobile porcelain	490
Mica plug	720		

* *Nat. Advisory Comm. Aeronautics*, 5th Ann. Report, 77-89, 1919.

Stoneware. Stoneware has a less specific resistivity than porcelain, but it enables much larger insulators to be made and is, therefore, a valuable material. Table XIV.XXIX shows the relative properties of porcelain and stoneware insulators.

TABLE XIV—XXIX. ELECTRIC INSULATORS

	Porcelain	Stoneware
Specific gravity	2.4	2.5
Expansion coefficient per 1° C.	0.000004	0.000003
Specific heat	0.2	0.2
Impact strength (ft. lb. per sq. in.)	1.6	1.5
Tensile strength (lb. per sq. in.)	3,000-6,000	4,300
Compressive strength (lb. per sq. in.)	30,000-65,000	60,000
Brinell hardness	700-1,500	10,000
Water absorption (by weight)	0.01%	0.03%
Oil absorption	Nil	Nil
Electric strength (volts per mil.)	200	95
Permittivity	4-6	—
Average power factor (at 130 kilocycles)	0.008	0.007

The electrical resistivity of some bricks is shown in Table XIV.XXX, due to Hartmann, Sullivan and Allen.²

TABLE XIV—XXX. ELECTRICAL RESISTIVITY
OF REFRACTORY BRICKS (ohms per cm.)

Temperature ° C.	Silica Bricks	Magnesite Bricks	Zirconia Bricks	Chromite Bricks	Silicon Carbide Bricks
Cold	Less than 125,000,000	Less than 137,000,000	Less than 134,000,000	Less than 48,000,000	Less than 127,000,000
800	2,380,000	5,000,000	558,000	803	835,000
900	765,000	1,240,000	224,000	525	477,000
1000	300,000	708,000	131,000	171	197,000
1100	126,000	560,000	53,800	78	75,000
1200	62,000	193,000	7,710	63	29,500
1300	30,900	67,400	2,100	77	15,200
1400	16,500	22,400	968	85	10,100
1500	8,420	2,500	412	41	8,590

² Hartmann, Sullivan and Allen, *J. Amer. Electrochem. Soc.*, 38, 279, 1920.

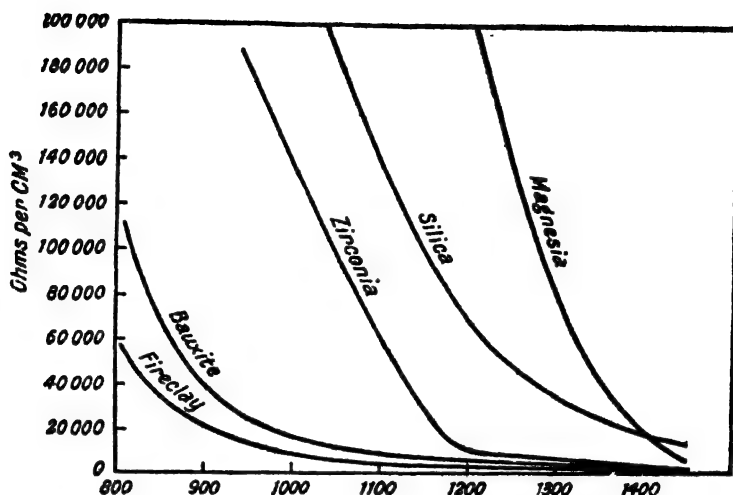


FIG. XIV.7. THE ELECTRICAL RESISTIVITY OF SOME REFRACTORY MATERIALS

Fig. XIV.7 (due to Hartman, Sullivan and Allen)¹ shows the electrical resistivity of various raw materials.

Fused silica has electrical insulating properties higher than those of glass and porcelain as shown in Table XIV.XXXI. According to tests at the National Physical Laboratory, silica glass has a specific inductive capacity of 3.5–3.6 and a dielectric strength of over 30,000 volts for a thickness of 1.2 mm. or 100–200 kilovolts per cm. for thicker specimens.

TABLE XIV—XXXI. COMPARATIVE RESISTIVITIES OF GLASSES

<i>Fused Silica</i>		<i>Soda-Lime Glass</i>		<i>Jena Glass</i>	
<i>Temp.</i> ° C.	<i>Resistivity</i> megohm-cm.	<i>Temp.</i> ° C.	<i>Resistivity</i> megohm-cm.	<i>Temp.</i> ° C.	<i>Resistivity</i> megohm-cm.
15	200,000,000	18	500,000	16	200,000,000
150	200,000,000	145	100	115 ¹	36,000,000
230	20,000,000			150	18,000,000
250	2,500,000			750	0.1–0.4
350	30,000				
450	800				
800	About 20				

Determination of Electrical Conductivity and Resistivity. The conductivity or resistivity of a material is usually determined on a centimetre cube of the sample which is placed between two electrodes. The current flowing when a high voltage is applied is measured and the resistivity calculated by simple application of Ohm's Law.

¹ *Trans. Amer. Electrochem. Soc.*, 38, preprint, 1920.

The *puncture-voltage* (i.e. the voltage required to break down the resistance and allow a current to pass readily) is generally determined by placing a sample of known thickness between two electrodes and applying a gradually increasing voltage until puncture or other breakdown occurs and noting the maximum voltage applied, the test piece being usually immersed in oil, unless the test is made at a high temperature, when oil cannot, of course, be used.

For details of other methods of determining the electrical properties of ceramic materials, Warren's *Electrical Insulators*, and other books should be consulted.

Surface Conductivity. In some cases, a material will have a high resistivity in volume, but will not behave so well in practice because of the ease with which electricity can pass through its surface layers. This arises principally as the result of the adsorption of a thin film of oil or water which acts as conducting layers. Materials with a smooth finish are less liable to break down in this way and for this reason a glaze or surface coating is usually applied. Silicones (organic silicon complexes) are being increasingly used for this purpose, because of their low water adsorption.

DIELECTRIC CONSTANT

AN electrical condenser is an arrangement of two parallel plates separated by a medium. The capacity of such a unit is governed largely by the nature of the intervening material and where high frequency alternating current is involved or high capacities required, it is important that the condenser plates be separated by a substance with a large *dielectric constant*.

A condenser may be regarded as a storehouse of electricity and the electrostatic capacity (C) of a parallel pair of electrodes of surface area A and separated by a small distance (d) is given by:

$$C = \epsilon \frac{A}{4\pi d}$$

where ϵ is a constant which depends upon the medium between the plates and is termed the *dielectric constant*.

Most of the commonly-employed solid electrical insulating materials, including paraffin wax, mica, glass and porcelain have dielectric constants of less than 10 (relative to air which is regarded as unity) and, furthermore, when subjected to alternating currents of high frequency such material becomes heated and the dielectric constant falls appreciably.

The addition of titanium dioxide to clay bodies increases the dielectric constant to about 60 and this discovery has led to the development of titanate bodies; barium titanate has a dielectric constant of about 1200 and when mixed with other ingredients, values of up to 10,000 have been attained. Above a certain temperature, known as the Curie temperature, such bodies lose their dielectric properties but additions of small amounts of zirconates, or stannates can increase their temperature stability.

Steatite bodies have a dielectric constant of about 60 and can withstand temperatures of up to 1000° C. without showing undue breakdown.

When certain substances are placed in an electric field, ionic alignments may be set up, thereby inducing *polarisation*. Usually there is a specific temperature above

which such substances lose their *ferroelectric* properties (the Curie temperature), but below this point the electric polarisation may be very high in some cases.

The dielectric constant (ϵ) of materials may be expressed by the equation:

$$\epsilon = 1 + 4\pi \frac{P}{E}$$

where P is the spontaneous electric polarisation and E is the applied electrical field.

The subject of ferro-electrics is outside the scope of this volume but it should be noted that some ceramic materials have remarkable properties in this respect. One such example is *perovskite* or barium titanate BaTiO_3 ; dielectric constants in excess of 10,000 are reported with this material as compared with figures of the order of 5 for rocksalt, quartz and similar materials. Materials of this type have also a large piezo-electric effect (p. 874).

LOW LOSS CERAMICS

MATERIALS which are used as insulators of alternating currents, tend to absorb energy which is dissipated as heat. This represents wasted energy and at the same time the electrical efficiency of the medium is reduced because of the attendant rise in temperature (see p. 878). When exposed to a high frequency alternating current, many of the standard insulating materials, such as porcelains and mica become excessively hot because they have a high *power factor*.

Ceramic bodies have been developed in which much less electrical energy is wasted; these include cordierite (talc + clay), clinoenstatite and steatite (or talc) (p. 336). Bodies containing titania (TiO_2) are also valuable for this purpose especially at higher frequencies; a rutile (TiO_2)—zirconia (ZrO_2) mixture has a power factor which is almost constant over a wide range of radio and electrical frequencies.

The composition of materials of value as insulators and dielectrics has been discussed in Chapter VI.

MAGNETIC PROPERTIES

SUBSTANCES which are magnetic have atoms, ions or electron fields which are oriented in such a way that dipole moments are set up within the crystals.

Clay, silica, most of the silicates, and many other ceramic materials are non-magnetic, but some of the impurities are susceptible to magnetic attraction, and, consequently, this property is sometimes used in their removal. Table XIV.XXXII shows the magnetic properties of different minerals.

Some burned fireclays are feebly magnetic on account of the presence of magnetic iron oxide or other minerals which are attracted by a magnet. All ferrous silicates are magnetic, and Zirkel found that fused phyllite ($\text{FeOAl}_2\text{O}_3\text{SiO}_2$) is also magnetic.

The magnetic properties of minerals, etc., may readily be determined by means of a small electro-magnet. A convenient one consists of two limbs, each 1 in. diameter and 4 in. long, wound with seven layers of 16-gauge wire, each layer having about forty turns. The two adjustable pole pieces should be $1\frac{1}{4}$ in. wide and

$\frac{1}{8}$ in. thick, slotted so as to be moved nearer to, or farther from, each other, and secured by screws to the limbs. An 8-volt battery is quite sufficient for this instrument. In use, the magnet is suspended over a cardboard tray containing the sample to be examined. If desired, the most magnetic particles may be removed with a permanent magnet, and the 'moderately magnetic' grains then removed by means of an electro-magnet, with its poles about $\frac{1}{4}$ in. apart. Afterwards, the poles of the magnet may be placed only $\frac{1}{4}$ in. or rather less apart and the 'feebly magnetic' minerals may then be separated. The residue may be regarded as practically non-magnetic. Alternatively, the minerals may be suspended in water, forming a slip, which can then be stirred with the magnet until all the magnetic particles have been removed.

TABLE XIV—XXXII. MAGNETIC PROPERTIES OF MINERALS

<i>Highly Magnetic</i>	<i>Moderately Magnetic</i>	<i>Feebly Magnetic</i>	<i>Almost Non-Magnetic</i>	
Magnetite	Hypersthene	Chlorite	Zircon	Rutile
Titanoferrite	Augite	Staurolite	Corundum	Barytes
Ilmenite	Garnet	Epidote	Galena	Most iron-free minerals
Pyrrhotite	Siderite	Limonite	Fluorspar	Clay
Haematite	Olivine	Actinolite	Pyrite	Silica
	Hornblende	Kyanite	Cassiterite	
	Chromite	Fayalite		

Magnets, arranged in series, are extensively used for removing minute particles of metallic iron from clay and body slips, these particles being largely derived from the machines used to grind the clay and other ingredients of the slips.

Recent developments in the field of electronics necessitate the use of materials which are ferro-magnetic and yet have a high electrical resistivity. The particular applications are as cores for coils and transformers carrying high frequency currents where energy is likely to be dissipated in the form of eddy currents. For a variety of reasons, ferrites are of great value in these applications and are now being used on an extensive scale. Ferrites differ widely in composition but they have all an identical crystal structure, based on the inverse spinel type discussed in Chapter IV. These materials owe their magnetic properties to the situation of cations in the lattice which behave as carriers of magnetic moments.

For a more detailed description of the properties of these and other ferro-magnetic materials, the reader is referred to other publications including those of Snoek,¹ Neel² and Merz.³

CHEMICAL PROPERTIES OF FIRED CERAMIC PRODUCTS

THE chief chemical properties of fired ceramic articles and other products are those which enable them to resist the chemical action of acids, alkalies and slags—the latter being a serious cause of *corrosion*.

¹ Snoek, J. L., *New Developments in Ferro-magnetic Materials* (Elsevier, New York, 1947).

² Neel, L., *Ann. de Physique*, 3, 137, 1948; *Comptes. Rendus.*, 230, 190, 1950.

³ Merz., W. J., 'Crystal Chemistry Symposium' (*Ceramic Age*, 1951).

Resistance to acids and alkalis is chiefly obtained in highly vitrified products such as some engineering bricks, stoneware and porcelains. When resistance to alkalis, lime, magnesia and slags is required at very high temperatures it is less feasible to use highly vitrified materials as they tend to fuse too readily; in such cases the density must be obtained by skilful grading of the raw materials so as to ensure close packing and so controlling the firing that no more glass is produced than is necessary.

Most ceramic materials are used because of their *inertness* to their contents (if hollow) or to their immediate surroundings. If they are unduly affected, they are either used unsuitably or are defective and should be dealt with accordingly.

CORROSION

CORROSION may be defined as a chemical, physical or electrolytic reaction between two or more components which results in the solution or disintegration of at least one of those components. The nature of the reactions may be similar to those involved in the firing of the raw material, but corrosion effects are, in general, undesirable and imply a reduction in the valuable properties of the ceramic material involved. Thus, the action of iron oxide on magnesia or of lime on silica may be useful, if in a small degree, in producing a suitable bond, but when these substances in excessive amounts attack refractory materials whilst the latter are in use, the effects are undesirable and may be included under the term 'corrosion'.

Many factors influence corrosion, some of which have been described on pp. 649-54. The principal ones are:

- (a) The available area of contact between the corroding agent and refractory.
- (b) The chemical affinity between the two reactants.
- (c) The mobility of the corroding agent.
- (d) The permeability or ease of penetration of the corroding agent into the ceramic material.

In some cases, the continued action of a corroding agent may, in time, prevent or hinder further action taking place. Thus, when calcium compounds attack fire-clay a calcium aluminosilicate is first formed which is high in calcium and has a low fusing point. As more clay is dissolved, the material formed becomes richer in alumina and silica and at the same time more refractory, so that in time a protective coating is formed and further corrosion is prevented or at least proceeds very slowly. There are five chief groups of substances which have a corrosive action on ceramic materials:

- (a) Free bases which combine directly with clay, silica, etc.
- (b) Silica, clay, and other materials which react like acids with basic refractory materials such as magnesite, etc.
- (c) Salts which, on heating, are decomposed, liberating a base and an acid, the base uniting with the fireclay, silica, or analogous refractory material and producing a fusible compound. To this class belong substances such as calcium sulphate, sodium chloride, etc. Thus, the soluble salts present in some coals used for making

gas or coke cause much trouble by corroding the material of which the retort or coke oven is made. Sodium chloride is usually the most important of these salts, though others may also be present.

(d) Direct-acting salts which act like free bases, though to a less degree. Felspar, mica, Cornish stone, and the carbonates are of this class.

(e) Fly ash and other corrosive substances carried in the hot gases in kilns, furnaces and ovens. These may be derived from the fuel or they may be picked up by the high velocity gas stream.

The chief corrosive agents to which clay, silica, and analogous materials are likely to be subjected are molten metals, slags, such as those produced in open-hearth, reverberatory, converting, and cupelling furnaces, consisting chiefly of basic materials or silicates (such as the slags produced in assaying), and metallic oxides. The action of volatilised substances may also be serious in some cases.

Lime should not be brought into contact with clay or silica at high temperatures or partial fusion may take place. Whiting (CaCO_3) attacks fireclay bricks in the same manner as lime, and so does Portland cement; the last-named, according to Hirsch, forms a calcium aluminosilicate, corresponding to the formula $2.5 \text{ CaAl}_2\text{O}_3 \cdot 3\text{SiO}_2$. The action is not so intense as that of lime or calcium carbonate.

Iron compounds form ferrous or ferric aluminosilicates, the former being more fusible and, therefore, more corrosive than the ferric compounds. Iron oxide corrodes fireclay bricks more severely than silica bricks. Sulphides are also very corrosive and rapidly penetrate clay products and silica. Iron sulphides are especially harmful in their action on these materials, because they combine with silica to form fayalite (FeOSiO_2) and sulphur dioxide which escapes as a gas. Any sulphur which may be present in the fuel used in furnaces may exert a corrosive action upon the brickwork at high temperatures, the sulphur being converted first into sulphur dioxide and then into sulphuric acid which attacks the bricks.

The presence of steam often facilitates the corrosive action of other substances; thus, its presence is necessary for the decomposition of some of the soluble salts in coal, and, for this reason, the preliminary drying of a coal may reduce the amount of corrosion of any firebricks with which it may be heated.

Fireclay bricks which are high in alumina are usually less easily corroded by fluxes, etc., than those rich in silica, but the amount or rate of corrosion is not always proportional to the total amount of alumina present. The solution of alumina by a slag containing a metasilicate may increase the fluidity of the slag and, therefore, increase its solvent action on bricks. With silicates richer in flux than metasilicates, however, the solution of alumina decreases the viscosity and increases the refractoriness of the bricks.

Howe, Phelps and Ferguson¹ have found that the resistance of some fireclay bricks to corrosion by slag is increased by a high alumina content, but some coal ashes (clinker) and some metallurgical slags attack highly aluminous bricks more readily than highly siliceous bricks.

¹ *J. Amer. Ceram. Soc.*, 6, 589, 1923.

Table XIV.XXXIII shows the refractoriness of various mixtures of slag and refractory material, obtained in the slag test devised by R. M. Howe, S. M. Phelps and R. F. Ferguson, in which the lowering of the refractoriness of a powdered mixture of slag and refractory material is regarded as the index of the intensity of the reaction.

Metallic vapours sometimes cause the destruction of firebricks. Thus, when vapours of metallic zinc penetrate the bricks of the blast furnaces in which the ores are smelted, they are oxidised by the CO_2 present and are solidified in the pores. This may cause disintegration if the bricks are not very strong. A similar corrosion occurs when zinc is smelted in retorts.

The penetration of vapours of sodium chloride into fireclay retorts may cause the formation of ferrous chloride which will, in turn, volatilise and act as a corrosive agent.

TABLE XIV—XXXIII. REFRACTORINESS OF MIXTURES OF SLAGS AND FIRECLAY BRICKS*

(The results are expressed in Seger Cones)

Type of Slag	Percentage of Slag in Mixture								
	0	4	8	12	16	20	30	40	50
Acid open-hearth	32	32	32	30	28	26	13	11	8
Blast furnace	32	30	29	20	17	13	13	12	9
Basic open-hearth	32	30	26	16	15	13	9	8	5
Heating furnace	32	31	30	26	19	18	10	9	8
Coal ash (clinker)	32	32	32	31	31	31	30	29	20

* The fireclay had an alumina content of 33 per cent.

Flue dust has a complex action upon firebricks producing a fusible mixture of various silicates and aluminosilicates, according to the composition of the dust. Mellor and Emery¹ determined the action of various corrosive flue dusts upon clays and siliceous refractory materials with the results shown in Table XIV.XXXIV.

Mellor and Emery found that the oxides of copper, zinc, and iron in a finely divided condition have a very high penetrative power under reducing conditions at very low temperatures. Copper oxide will penetrate at 600° C. and iron at 1100° C. They found tap cinder to be the most corrosive dust amongst those they examined, though the dust from the slag chamber of a steel furnace is extremely corrosive.

Carbon monoxide and some hydrocarbon gases are decomposed by hot fireclay with the deposition of carbon in the pores. The latter may rupture the bricks. In some circumstances the presence of less than $\frac{1}{2}$ per cent of carbon in a fireclay brick causes its disintegration. When no disintegration occurs, a superficial deposition of carbon on refractory articles is sometimes an advantage, as it may protect them and prevent wear and corrosion.

The texture of fireclays largely influences the degree of resistance to erosion. A low-grade fireclay, for example, which has been fired to a temperature at which

¹ *Trans. Eng. Ceram. Soc.*, 18, 230, 1918–19.

extensive vitrification occurs may be more resistant to metal or slag penetration than a clay of higher grade fired at the same temperature. The low refractory clay readily forms a protective glassy coat on its surface when in contact with the slag and thereby prevents the penetration of the corrosive agent along the pores of the material. Similarly, a brick with an initially low permeability is less liable to corrosive action than one where the penetration may be high.

TABLE XIV—XXXIV. CORROSIVE ACTION OF VARIOUS FLUE DUSTS

	<i>Firebrick</i>	<i>Silica Bricks</i>	<i>Fine-grained Silica Brick</i>
Boiler flue dust high in lime and ferric oxide	dP mC	—	—
Ferruginous boiler flue dust	sP sC	—	—
Ochreous dust from retort brick	kP sC	dP gC	—
Basic slag	dP sC	dP mC	—
Ferruginous dust high in lime	kP mC	dP mC	—
Bull dog	—	dP sC	—
Haematite (reducing flame)	—	dP sC	sP sC
Tap cinder	dP mC	dP mC	dP sC
Lime	sP mC	sP mC	—
Lime and salt	sP mC	sP mC	—
Salt	dP sC	sP mC	—
Sodium sulphate	sP sC	sP mC	—
Salt and felspar	sP sC	sP mC	—
Soda lime-glass	sP sC	sP mC	—

P = penetration

s = slight

d = deep

gC = great corrosion or slagging

k = complete

m = medium

C = corrosion

Clays which bloat at high temperatures are often extremely resistant to corrosion probably because the increase in size is sufficient to seal surface pores and to reduce the sizes of the joints between adjacent bricks. Such bricks are commonly used, especially in the U.S.A. as linings for steel ladles. In general, siliceous clays are more readily corroded than others due to the greater ease with which they form a liquid.

Aluminous clays are less liable to be attacked and this may be due in no small part to the ease with which they form *mullite*, which is extremely stable and is not readily decomposed.

Silica bricks are in theory more reactive to basic slags at high temperatures than are fireclays, but the amount of attack depends on the texture. The penetration of slags into a siliceous refractory is through the glass which surrounds the crystallites of cristobalite and tridymite, or along pores and fissures leading from the surface; a close-textured brick and one containing little glass is much less readily attacked. The action of lime and iron oxide on silica at high temperatures is not as pronounced as would be expected from a combination of bases and acids. As shown in Figs. X.18, 19, 20 (p. 563) oxides of iron, calcium and magnesium form an immiscible

liquid phase with silica and for this reason a large proportion of these oxides can be absorbed in a silica brick without an undue deterioration in property occurring. If small amounts of alumina are present as an impurity, the reaction is very rapid and the brick readily disintegrates.

The permeability of a silica brick has a pronounced influence on its corrosion resistance to dusts and slags at high temperature. Bricks made from silcrete (p. 316) contain a larger proportion of impurities than do refractories made from silica rock. The porosity of the former is only about half that of the bricks made from quartzites, consequently the slagging action is confined largely to the surface and does not readily penetrate along the pores. For this reason, silcrete bricks are far more resistant to corrosion than those made from high quality quartzite.

Fused silica has a high resistance to attack by most chemicals and because it also has a high resistance to thermal shock it is a valuable material in chemical plants and in laboratory apparatus. It is rapidly attacked by hydrofluoric acid and should not be kept in contact with alkali.

Magnesite, dolomite, chrome and chrome-magnesite bricks are basic in character and are consequently more resistant to basic slags than are silica and fireclay bricks. Components of such slags, however, combine readily with the matrix minerals of such bricks and form low melting compounds (p. 694) which cause disintegration.

Chrome-magnesite refractories, because the gangue material is essentially forsterite are less liable to the penetration of slags. The spinel crystals which form the greater part of the refractory are attacked by iron oxide. The action is still not completely explained although apparently iron oxide Fe_3O_4 is isomorphous with certain spinels and can form solid solutions giving rise to a large volume expansion. This 'iron-oxide bursting' may be very severe and limits the use of some chrome-magnesite bricks in many industrial and metallurgical applications.

Aluminous bricks and those made from kyanite are moderately resistant to most slags—the rate of attack is very dependent on the texture.

Zircon and zirconia bricks and crucibles are highly resistant to slags and consequently they are very valuable refractories. They withstand the corrosive action of acid slags, liquid glasses of various kinds, most molten metals and some basic slags. Zircon refractories have been used in gas retorts where the attack by iron oxide at high temperatures is very severe and have proved successful, but their high cost limits their use.

Carbon bricks are extremely resistant to molten slags and metals of all types. They are serviceable at high temperatures, however, only in the absence of air.

Silicon carbide is also highly resistant to most slags and molten metals.

Measurement of Corrosion. The usual method for measuring the resistance of ceramic materials to slags is to drill a hole 1 in. diameter and $\frac{1}{2}$ in. deep in a block 3 in. \times 2 in. \times 2 in. cut from a brick. This recess is filled with a powdered sample of the slag and the block fired to the normal contact temperature between the slag and the refractory material. After the maximum temperature has been maintained for two hours, the furnace is cooled and the block cut vertically to show the depth of penetration.

Chesters¹ has described a slag spray test in which powdered slag is fed into the flame from a gas burner and then sprayed on to a panel of the bricks under test. The extent of penetration and the wear on the bricks are then measured.

Howe, Phelps and Ferguson² suggest that the resistance of refractory materials to the action of slag may be tested by powdering the bricks and slag so that they will pass completely through an 80-mesh sieve, mixing them in various proportions, and determining the refractoriness of the mixtures. They claim that this method more nearly agrees with the conditions observed in works' practice, the chief of these being (a) increased intensity of action with increased slag concentration; (b) the different action of different slags; and (c) the effect of any slag on different refractory materials.

Although this method is of value in indicating the probable nature of the chemical attack during corrosion it takes no account of the texture of the ceramic material which is often more important than its chemical nature.

Partridge and others measure the corrosive effect of glass on clay by immersing a specimen of the clay (15 mm. sq. section) in a porcelain crucible containing the molten glass for a suitable time, afterwards cutting the specimens and polishing. The change in the size of the specimen is measured and the polished surface is examined under a low-power microscope.

Mackenzie³ has devised a similar simple but highly satisfactory comparison test for measuring the relative erosion rate of ladle materials in the hot metal. A long bar of 1 in. square end section is partly lowered into a crucible of the hot metal. After a certain time interval it may be withdrawn and the amounts of corrosion assessed.

¹ Chesters, J. H., *Steelplant Refractories* (The United Steel Companies Ltd., Sheffield, 1957).

² Howe, R. M., Phelps, S. M. and Ferguson, R. F., *J. Amer. Ceram. Soc.*, 6, 589, 1923.

³ Mackenzie, J., *Trans. Brit. Ceram. Soc.*, 53, 654, 1954.

NOTES TO THE APPENDIX

1. The optical values have either been determined by the author or are taken from the collected data of Winchell¹ and Rigby².

2. (a) The X-ray data for ceramic minerals are largely from the author's collection, supplemented by data published by the American Society for Testing Materials.

(b) In most cases, the three lines quoted are the strongest of those given by a particular mineral, but where necessary, the characteristic lines by which a mineral may be identified are preferentially quoted. Where minerals have been arranged in families, reflections from equivalent spacings are compared irrespective of their relative intensities.

(c) The values of the intensity of lines are relative to the intensity (10) of the strongest line for a particular mineral.

3. (a) Differential thermal analysis data have been derived by using purified minerals from reputable sources, tested by the standard method described in Chapter V.

(b) The absence of values of thermal effects for certain minerals does not necessarily mean that those minerals are unreactive. Undoubtedly, some minerals undergo polymorphic transformations when heated which would be manifested as a small thermal effect capable of detection by more sensitive equipment. These have not been included in the present survey, nor have thermal effects about which there is a reasonable doubt.

(c) The magnitudes of thermal effects are classified as :

v. large	—						producing a temperature difference greater than 90° C.
large	—	„	„	„	„	„	50° C.
medium	—	„	„	„	„		between 10–50° C.
small	—	„	„	„	„		less than 10° C.
v. small	—	„	„	„	„	„	3° C.

¹ Winchell, A. N. see p. 217.

² Rigby, G. R., see p. 217.

OPTICAL PROPERTIES

	Composition	Crystal system	Specific gravity	Hardness	Refractive index	Birefringence	Interference figure	Crystal habit	Colour
Clay and Related Minerals									
1. kaolinite	$\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_2$	Triclinic	2.61	2	1.56	0.006	B-neg.	Plates	None
2. halloysite (normal)	$\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_2$	Hexagonal?	2.62	—	1.52	0.030	B-neg.	Small needles	None
3. livesite	$\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_2$	Monoclinic	2.63	—	1.54	0.020	B-neg.	Small plates	Yellow?
4. dickite	$\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_2$	Monoclinic	2.62	2.5	1.56	0.006	B-neg.	Plates	None
5. nacrite	$\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_2$	Orthorhombic	2.54	2.5	1.56	0.006	B-neg.?	Plates	None
6. anauxite	$\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot 2\text{H}_2\text{O}$	—	2.60	—	—	—	—	—	—
7. allophane	$\text{Al}_2 \cdot 1.5\text{SiO}_2 \cdot n\text{H}_2\text{O}$	—	—	—	1.49	—	Isotropic	—	—
8. montmorillonite	$(\text{Al}, \text{Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2$	Monoclinic	2.5	2	1.51	0.021	B-neg.	Small flakes	None
9. beidellite	$\text{Al}_2(\text{Al}, \text{Si})_4\text{O}_{10}(\text{OH})_2$	Monoclinic	2.5	2	1.51	0.020	B-neg.	Small flakes	Cream
10. nontronite	$(\text{Al}, \text{Fe}, \text{Mg})_2(\text{Al}, \text{Si})_4\text{O}_{10}(\text{OH})_2$	Monoclinic	2.6	2	1.56	0.023	B-neg.	Small laths	Brown
11. hectorite	$(\text{Mg}, \text{Li}, \text{Al})_2\text{Si}_4\text{O}_{10}(\text{OH})_2$	Monoclinic	2.4	2	1.49	0.022	B-neg.	Small flakes	None
12. saponite	$\text{Mg}_2(\text{Al}, \text{Si})_4\text{O}_{10}(\text{OH})_2$	Monoclinic	2.5	2	1.50	0.015	B-neg.	Small flakes	None
13. talc	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	Monoclinic	2.75	1	1.58	0.040	B-neg.	Plates	None
14. pyrophyllite	$\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$	Monoclinic	2.80	1.5	1.57	0.050	B-neg.	Plates	None
15. vermiculite	$(\text{Mg}, \text{Fe})_2(\text{Al}, \text{Si})_4\text{O}_{10}(\text{OH})_2$	Monoclinic	2.4	1.5	1.56	0.020	B-neg.	Plates	Brown
16. glauconite	$\text{KMg}(\text{Fe}, \text{Al})_2\text{Si}_4\text{O}_{10} \cdot 3\text{H}_2\text{O}$	Monoclinic	2.4	2	1.60	0.020	B-neg.	Small laminae	(Red) Green
17. sepiolite	$\text{H}_2\text{Mg}_2\text{Si}_4\text{O}_{10} \cdot n\text{H}_2\text{O}$	Orthorhombic	2	2	1.53	0.010	U-neg.	Small fibrous	None
18. palygorskite (attapulgite)	$\text{Mg}_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$	Orthorhombic	—	—	1.51	0.020	—	Small fibrous	—

X-RAY ANALYSIS

DIFFERENTIAL THERMAL ANALYSIS
(Grimshaw and Roberts Apparatus)

Three principal lines						Endothermic Peaks (maxima)		Exothermic Peaks (maxima)		
<i>d</i> in Å ; <i>I</i> , relative intensity						Temp. °C.	Magnitude	Temp. °C.	Magnitude	
<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>					
7.15	10 +	3.566	10 +	2.331	10	105 585	small large	985	v. large	1
7.2	8	3.566	8	4.422	10 +	115 550	medium large	985	large	2
7.15	10	3.566	10	4.455	8	110 200? 553	medium small large	925-945	medium	3
7.14	10	3.576	10 +	2.318	8	105 580 695	v. small small large	980	large	4
7.08	10	3.58	9	2.418	10	105 690	v. small large	980	large	5
7.1	10	3.57	10	2.35	10	105 580	v. small large	980	large	6
—	—	—	—	—	—	200 520	medium small	985	medium	7
14.7	10	4.42	5	1.49	4	140 700 875	medium medium small	920	small	8
14.2	10	4.45	4	1.49	4	150 540	medium small	915	small	9
14.0	10	4.48	3	1.51	2	140 490	medium medium	900	small	10
14.3	10	4.44	3	1.51	5	145 840	medium medium	—	—	11
14.0	10	4.51	5	1.52	5	150 870	medium medium	—	—	12
9.30	8	3.10	10	1.53	8	910	medium (broad)	—	—	13
9.14	8	3.06	10	1.50	8	750	medium (broad)	—	—	14
14.1	10	3.54	6	1.53	6	120-200 820	medium small	860	small	15
9.92	10	4.45	9	3.34	9	110 565 895	small medium small	920	medium	16
12.15	10	4.60	10	2.61	8	140 810	medium medium	300-600 880	medium (broad) medium	17
10.5	10	4.49	8	3.23	10	110 260 410 535	small medium medium small	940	medium	18

OPTICAL PROPERTIES

	Composition	Crystal system	Specific gravity	Hardness	Refractive index	Birefringence	Interference figure	Crystal habit	Colour
Micas									
19. muscovite	$\text{KA1}_2(\text{Al}_1\text{Si}_4)\text{O}_{10}(\text{OH})_2$	Monoclinic	2.9	2.5	1.59	0.036	B-neg.	Plates	None
20. paragonite	$\text{NaAl}_2(\text{Al}_1\text{Si}_4)\text{O}_{10}(\text{OH})_2$	Monoclinic	2.9	2.5	1.60	0.030	B-neg.	Plates	None
21. lepidolite	$\text{K}(\text{Li}, \text{Al})_2(\text{Al}_1\text{Si}_4)\text{O}_{10}(\text{OH})_2$	Monoclinic	3.0	3	1.56	0.020	B-neg.	Plates	None
22. biotite	$\text{K}(\text{Mg}, \text{Fe})_2(\text{Al}_1\text{Si}_4)\text{O}_{10}(\text{OH})_2$	Monoclinic	3.1	2.5	1.63	0.050	B-neg.	Plates	Brown
23. margarite	$\text{CaAl}_2(\text{Al}_1\text{Si}_4)\text{O}_{10}(\text{OH})_2$	Monoclinic	3.0	4	1.65	0.010	B-neg.	Tabular	None
24. hydrous mica	Variable	Monoclinic	2.75	—	1.57	0.021	B-neg.	Plates	None
Feldspars									
25. orthoclase	$\text{KA1 Si}_3\text{O}_8$	Monoclinic	2.55	6	1.52	0.006	B-neg.	Prismatic	None
26. microcline	$\text{KA1 Si}_3\text{O}_8$	Triclinic	2.55	6	1.53	0.007	B-neg.	Equant	None
27. celsian	$\text{BaAl}_2\text{Si}_2\text{O}_8$	Monoclinic	3.4	6	1.59	0.010	B-pos.	Prismatic	None
28. albite	$\text{NaAlSi}_3\text{O}_8$	Triclinic	2.61	6	1.53	0.010	B-pos.	Tabular	None
29. andesine	$(\text{Na}, \text{Ca})(\text{Al}, \text{Si})_3\text{O}_8$	Triclinic	2.67	6	1.55	0.007	B-pos.	Tabular	None
30. anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8$	Triclinic	2.76	6	1.58	0.013	B-neg.	Tabular	None
Felspathoids									
31. leucite	$\text{KA1 Si}_4\text{O}_{12}$	Orthorhombic	2.47	6	1.51	0.001?	Iso-tropic?	Equant	None
32. nephelite	$\text{NaAl Si}_4\text{O}_{12}$	Hexagonal	2.61	6	1.54	0.004	U-neg.	Prismatic	None
33. carnegieite	$\text{NaAl Si}_4\text{O}_{12}$	Triclinic	2.51	6	1.51	0.005	B-neg.	Needle	None
34. eucryptite	$\text{LiAlSi}_4\text{O}_{12}$	Hexagonal	2.67	—	1.55	0.002	U-neg.	Prismatic	None
Chlorites									
35. antigorite	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	Orthorhombic	2.57	3.5	1.57	0.008	B-neg.	Fibrous	Green
36. amesite	$(\text{Mg}, \text{Al})(\text{AlSi})_3\text{O}_{10}(\text{OH})_2$	Monoclinic	2.8	2.5	1.58	0.015	B-pos.	Lamellae	Pale green
37. daphnite	$(\text{Fe}, \text{Al})(\text{Al}, \text{Si})_3\text{O}_{10}(\text{OH})_2$	Monoclinic	3.0	2	1.65	0.001	B-neg.	Lamellae	Green

X-RAY ANALYSIS

DIFFERENTIAL THERMAL ANALYSIS
(Grimshaw and Roberts Apparatus)

Three principal lines						Endothermic Peaks (maxima)		Exothermic Peaks (maxima)		
<i>d</i> in Å; <i>I</i> , relative intensity						Temp. °C.	Magnitude	Temp. °C.	Magnitude	
<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>					
9.98	10	3.33	9	2.57	10	600-900	small (broad)	—	—	19
9.97	6	4.41	10*	3.10	10	—	—	—	—	20
9.84	5	4.42	10	3.60	10	750	medium	—	—	21
10.1	10	3.36	9	2.65	7	550 700-900	medium small (broad)	—	—	22
—	—	—	—	—	—	—	—	—	—	23
10.0	10	4.45	8	3.32	9	105 550 625-660	v. small small medium	940	medium	24
3.20	10	1.81	9	4.02	8	850	small (broad)	—	—	25
3.21	10	1.80	8	2.16	6	—	—	—	—	26
2.60	10	2.09	8	1.79	7	—	—	—	—	27
3.20	10	1.80	6	4.00	5	820	medium	—	—	28
3.19	10	1.88	6	4.00	5	—	—	—	—	29
3.17	10	2.51	6	4.02	4	780	medium	—	—	30
3.27	10	5.30	9	3.42	8	640	v. small	—	—	31
3.01	10	3.82	9	3.17	8	—	—	—	—	32
4.29	10	2.61	9	1.50	6	690	v. small	—	—	33
3.97	10	2.55	10	6.92	8	440	v. small	—	—	34
7.14	9	3.59	10	2.52	7	105 640	v. small large	840	large	35
7.0	10	3.50	10	2.47	9	105 580	v. small medium	780	small	36
6.9	8	3.51	10	4.69	5	105 460-600	v. small medium (broad)	780	small	37

OPTICAL PROPERTIES

	Composition	Crystal system	Specific gravity	Hardness	Refractive index	Birefringence	Interference figure	Crystal habit	Colour
38. ferro-antigorite	$\text{Fe}_2\text{Si}_4\text{O}_8(\text{OH})_4$	Monoclinic	3.2	2	1.66	0.007	B-neg.	Lamellae	Dark green
39. penninite	$(\text{Mg}, \text{Fe}, \text{Al})_2(\text{Al}, \text{Si})_2\text{O}_4(\text{OH})_4$	Monoclinic	2.70	2	1.57	0.002	B-pos.?	Lamellae	Green
40. chrysotile (serpentine)	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$	Orthorhombic	2.42	2.5	1.55	0.013	B-pos.	Fibrous	Green
Olivines									
41. forsterite	Mg_2SiO_4	Orthorhombic	3.22	6.5	1.67	0.035	B-pos.	Equant	None
42. fayalite	Fe_2SiO_4	Orthorhombic	4.32	6.5	1.88	0.051	B-neg.	Equant	Green, red
43. chrysolite	$(\text{Mg}, \text{Fe})_2\text{SiO}_4$	Orthorhombic	3.3	6.5	1.68	0.035	B-pos.	Prismatic	Green
44. monticellite	CaMgSiO_4	Orthorhombic	3.2	5	1.64	0.017	B-pos.?	Prismatic	None
Pyroxenes									
45. enstatite	MgSiO_3	Orthorhombic	3.18	5.5	1.65	0.004	B-pos.	Prismatic	None
46. clinoenstatite	MgSiO_3	Monoclinic	3.19	5.5	1.65	0.004	B-pos.	Prismatic	None
47. diopside	$(\text{CaMg})\text{SiO}_3$	Monoclinic	3.28	5	1.66	0.032	B-pos.	Prismatic	None
48. augite	$(\text{Ca}, \text{Mg}, \text{Fe})\text{SiO}_3$	Monoclinic	3.4	5.5	1.71	0.026	B-neg.	Prismatic	Green, brown
49. spodumene	$(\text{LiAl})\text{SiO}_3$	Monoclinic	3.15	6.5	1.68	0.027	U-pos.	Prismatic	None
50. wollastonite	$(\text{Fe}, \text{Ca})\text{SiO}_3$	Triclinic	2.92	4.5	1.61	0.020	B-neg.	Needles	Pale green
Amphiboles									
51. tremolite	$\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$	Monoclinic	3.1	5.5	1.62	0.026	B-neg.	Fibrous	None
52. hornblende	$\text{Ca}_2\text{Na}(\text{Mg}, \text{Fe}, \text{Al})_6\text{Al}_2\text{Si}_4\text{O}_{22}(\text{OH})_2$	Monoclinic	3.3	5.5	1.68	0.019	B-neg.	Fibrous	Green, brown
Melilites									
53. akermanite	$\text{Ca}_2\text{MgSi}_2\text{O}_7$	Tetragonal	3.18	5	1.63	0.007	U-pos.	Prismatic	None
54. gehlenite	$\text{Ca}_2\text{Al}(\text{SiAl})_2\text{O}_7$	Tetragonal	3.04	5.5	1.67	0.010	U-neg.	Prismatic	None

X-RAY ANALYSIS

DIFFERENTIAL THERMAL ANALYSIS
(Grimshaw and Roberts Apparatus)

Three principal lines						Endothermic Peaks (maxima)		Exothermic Peaks (maxima)		
<i>d</i> in Å ; <i>I</i> , relative intensity						Temp. °C.	Magnitude	Temp. °C.	Magnitude	
<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>					
7.12	10	3.50	10	2.63	4	110 480	small large	760	medium	38
14.3	6	7.17	10	4.78	10	105 650 810	small large small	840	medium	39
7.07	4	3.59	10	2.45	6	105 635 800	v. small large small	850	medium	40
1.74	10	3.89	5	2.49	5	—	—	—	—	41
1.76	4	3.71	4	2.85	10	—	—	—	—	42
1.75	10	2.46	10	2.52	10	—	—	—	—	43
1.81	9	1.59	10	2.65	7	—	—	—	—	44
3.16	10	2.86	7	1.48	6	—	—	—	—	45
3.16	10	2.87	9	1.52	8	—	—	—	—	46
3.0	10	2.51	8	1.62	6	—	—	—	—	47
2.98	10	2.52	9	1.62	9	—	—	—	—	48
2.90	10	2.75	9	4.35	7	—	—	—	—	49
2.98	10	3.30	8	1.75	7	—	—	—	—	50
3.30	10	1.56	10	4.61	8	—	—	—	—	51
8.80	10	1.44	10	2.70	8	—	—	—	—	52
2.85	10	1.76	8	1.38	7	—	—	—	—	53
2.82	10	1.75	7	1.39	6	—	—	—	—	54

OPTICAL PROPERTIES

	Composition	Crystal system	Specific gravity	Hardness	Refractive index	Birefringence	Interference figure	Crystal habit	Colour
Alumino-silicates									
55. sillimanite	$\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$	Orthorhombic	3.08	7.5	1.66	0.022	B-pos.	Fibrous	None
56. andalusite	$\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$	Orthorhombic	3.18	7.5*	1.63	0.010	B-neg.	Prismatic	None
57. kyanite	$\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$	Triclinic	3.59	7.5	1.71	0.011	B-neg.	Tabular	None
58. mullite	$3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	Orthorhombic	3.03	7.5	1.65	0.012	B-pos.	Needles	None
Misc. Silicates									
59. zircon	Zr SiO_4	Tetragonal	4.5	7.5	1.93	0.053	U-pos.	Prismatic	None
60. phenacite	$\text{Be}_2 \text{SiO}_4$	Rhombohedral	3.0	7.5	1.65	0.016	U-pos.	Prismatic	None
61. topaz	$(\text{Al}, \text{F})_2 \text{SiO}_4$	Orthorhombic	3.55	8	1.62	0.010	B-pos.	Prismatic	None
62. beryl	$\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$	Hexagonal	2.71	7.5	1.57	0.006	U-neg.	Prismatic	None
63. cordierite	$\text{Al}_2\text{Mg}_2(\text{Si}_2\text{Al})\text{O}_{10}$	Orthorhombic	2.6	7	1.54	0.008	B-neg.	Prismatic	None
64. tourmaline	Complex silicate of B + Al + other cations	Hexagonal	3.0	7	1.67	0.029	U-neg.	Prismatic	Blue
65. titanite (sphene)	$\text{CaTiO}_5 \cdot \text{SiO}_2$	Monoclinic	3.5	5	1.99	0.110	B-pos.	Plates	Brown, green
66. merwinite	$\text{Ca}_2 \text{Mg} (\text{SiO}_3)_2$	Monoclinic	3.15	6	1.71	0.010	B-pos.	Prismatic	None
Oxides									
67. quartz (α)	SiO_2	Hexagonal	2.65	7	1.55	0.009	U-pos.	Prismatic	None
68. cristobalite (α)	SiO_2	Tetragonal	2.32	7	1.48	0.003	U-neg.?	Octahedral mosaic	None
69. tridymite (α)	SiO_2	Orthorhombic	2.28	7	1.47	0.004	B-neg.	Laths 'twinned'	None
70. opal	$\text{SiO}_2 \cdot n\text{H}_2\text{O}$	Amorphous	2.1	6	1.45	—	Iso-tropic	Pebbles	Milky
71. chalcedony	SiO_2	Hexagonal?	2.6	6	1.53	0.007	?	Fibrous	None
72. anatase	TiO_2	Tetragonal	3.9	6	2.55	0.073	U-neg.	Prismatic	Brown
73. rutile	TiO_2	Tetragonal	4.2	6	2.89	0.275	U-pos.?	Fibrous	Red
74. brookite	TiO_2	Orthorhombic	4.0	6	2.64	0.108	B-pos.	Prismatic	Brown
75. ilmenite	Fe Ti O_2	Hexagonal	4.7	7	—	—	—	Lamellar	Opaque black

X-RAY ANALYSIS

DIFFERENTIAL THERMAL ANALYSIS
(Grimshaw and Roberts Apparatus)

Three principal lines						Endothermic Peaks (maxima)		Exothermic Peaks (maxima)		
<i>d</i> in Å; <i>I</i> , relative intensity						Temp. °C.	Magnitude	Temp. °C.	Magnitude	
<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>					
3.39	10	2.20	9	1.52	7	—	—	—	—	55
4.58	10	1.48	10	2.17	8	—	—	—	—	56
1.95	10	1.38	10	3.20	10	—	—	—	—	57
3.42	10	2.21	8	1.53	8	—	—	—	—	58
3.29	10	2.52	9	1.71	7	—	—	—	—	59
3.11	10	2.52	8	1.26	8	—	—	—	—	60
2.96	10	1.40	10	1.38	9	—	—	—	—	61
8.10	10	3.33	8	2.92	8	—	—	—	—	62
8.29	7	3.33	8	3.0	10	—	—	—	—	63
2.59	10	6.50	8	3.48	8	—	—	—	—	64
3.20	10	2.59	10	2.98	9	—	—	—	—	65
1.90	10	2.68	6	1.53	6	—	—	—	—	66
3.35	10	1.814	8	4.21	7	573	v. small	—	—	67
4.05	10	2.48	9	2.85	5	220-280	v. small	—	—	68
4.30	10	4.10	8	3.80	7	117 163	v. small v. small	—	—	69
—	—	—	—	—	—	220 1250	small small	—	—	70
—	—	—	—	—	—	1250	small	—	—	71
3.51	10	1.89	9	1.70	7	—	—	—	—	72
3.24	10	1.36	8	1.69	10	—	—	—	—	73
3.47	10	1.88	8	2.90	10	—	—	—	—	74
2.75	10	2.54	8	3.73	7	650	small	—	—	75

OPTICAL PROPERTIES

	Composition	Crystal system	Specific gravity	Hardness	Refractive index	Birefringence	Interference figure	Crystal habit	Colour
76. corundum	Al_2O_3	Hexagonal	4.03	9	1.77	0.008	U-neg.	Angular	None
77. haematite	Fe_2O_3	Hexagonal	5.2	5	3.0	0.21	U-neg.	Platy	Brown
78. periclase	MgO	Cubic	3.65	6	1.74	—	Iso-tropic	Equant	None
79. baddeleyite	ZrO_2	Monoclinic	5.7	6.5	2.20	0.070	B-neg.	Tabular	None
80. cassiterite	SnO_2	Tetragonal	6.9	6	2.0	0.097	U-pos.	Prismatic	Brown
81. perovskite	Ca Ti O_3	Cubic	4.0	5.5	2.34	—	Iso-tropic	Cubes	Yellow Green
82. chrysoberyl	$\text{Be Al}_2 \text{O}_4$	Orthorhombic	3.64	8.5	1.75	0.004	B-pos.	Tabular	
Spinel									
83. spinel	$\text{Mg Al}_2 \text{O}_4$	Cubic	3.6	8	1.72	—	Iso-tropic	Equant	None
84. chromite	$\text{Fe Cr}_2 \text{O}_4$	Cubic	4.5	5.5	2.12	—	Iso-tropic	Equant	Orange
85. magnetite	$\text{Fe Fe}_2 \text{O}_4$	Cubic	5.2	6	2.42	—	Iso-tropic	Equant	Opaque black
Hydroxides									
86. diaspor	AlO (OH)	Orthorhombic	3.4	7	1.75	0.048	B-pos.	Prismatic	None
87. gibbsite	Al (OH)_3	Monoclinic	2.35	3	1.59	0.020	B-pos.	Tabular	None
88. goethite	FeO (OH)	Orthorhombic	4.28	5	2.40	0.140	B-pos.	Prismatic	Brown
89. brucite	Mg (OH)_2	Hexagonal	2.4	2.5	1.58	0.019	U-pos.	Tabular	None
Sulphates									
90. anhydrite	Ca SO_4	Orthorhombic	2.9	3	1.61	0.044	B-pos.	Prismatic	None
91. celestite	Sr SO_4	Orthorhombic	4.0	3.5	1.63	0.009	B-pos.	Tabular	None
92. barite	Ba SO_4	Orthorhombic	4.5	3	1.65	0.012	B-pos.	Tabular	None
93. anglesite	Pb SO_4	Orthorhombic	6.3	3	1.89	0.017	B-pos.	Tabular	None
94. mirabilite (glauher salt)	$\text{Na}_2 \text{SO}_4 \cdot 10\text{H}_2\text{O}$	Monoclinic	1.46	1.5	1.44	0.001	B-neg.	Fibrous	None
95. epsomite	$\text{Mg SO}_4 \cdot 7\text{H}_2\text{O}$	Orthorhombic	1.68	2	1.46	0.028	B-neg	Prismatic	None

X-RAY ANALYSIS

DIFFERENTIAL THERMAL ANALYSIS
(Grimshaw and Roberts Apparatus)

Three principal lines						Endothermic Peaks (maxima)		Exothermic Peaks (maxima)		
<i>d</i> in Å; <i>I</i> , relative intensity						Temp. °C.	Magnitude	Temp. °C.	Magnitude	
<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>					
2.08	10	1.60	10	2.55	9	—	—	—	—	76
2.69	10	2.51	8	1.69	8	—	—	—	—	77
2.10	10	1.49	7	1.21	2	—	—	—	—	78
3.19	10	2.85	8	1.81	4	—	—	—	—	79
3.32	10	2.62	10	1.75	10	—	—	—	—	80
2.70	10	1.91	8	1.56	7	—	—	—	—	81
2.08	10	1.61	10	3.24	8	—	—	—	—	82
2.41	10	1.42	10	4.62	8	—	—	—	—	83
2.51	10	1.46	8	3.10	4	—	—	—	—	84
2.53	10	1.48	7	2.96	6	325 620	small small	—	—	85
3.98	10	2.31	8	1.63	8	550	large	—	—	86
4.83	10	4.34	6	3.30	3	240 305 520	small v. large medium	—	—	87
4.15	10	2.43	7	2.67	6	335	large	—	—	88
4.75	8	2.36	10	1.79	4	435	large	—	—	89
1.85	10	3.49	10	2.79	7	1020	medium	—	—	90
2.04	10	3.32	10	2.97	10	1025	medium	—	—	91
2.11	10	3.42	8	3.09	8	1045	medium	—	—	92
2.07	10	4.24	9	3.0	7	900	medium	—	—	93
3.10	10	2.77	10	4.62	8	145 880	v. large medium	—	—	94
4.40	10	2.92	6	4.04	3	200 320 920	large medium medium	—	—	95

OPTICAL PROPERTIES

	Composition	Crystal system	Specific gravity	Hardness	Refractive index	Birefringence	Interference figure	Crystal habit	Colour
96. gypsum	$\text{Ca SO}_4 \cdot 2\text{H}_2\text{O}$	Monoclinic	2.32	2	1.53	0.009	B-pos.	Tabular	None
97. plaster of Paris	$2\text{Ca SO}_4 \cdot \text{H}_2\text{O}$	Monoclinic	2.5	2	1.55	0.020	B-pos.?	Tabular	None
98. alunite	$\text{KA l}_3(\text{OH})_4(\text{SO}_4)_3$	Rhombohedral	2.60	4	1.57	0.020	U-pos.	Cubic	None
Carbonates									
99. magnesite	Mg CO_3	Rhombohedral	2.96	3.5	1.70	0.191	U-neg.	Equant	None
100. siderite	Fe CO_3	Rhombohedral	3.85	3.5	1.87	0.242	U-neg.	Equant	Gray, brown
101. calcite	Ca CO_3	Rhombohedral	2.71	3	1.65	0.170	U-neg.	Equant	None
102. dolomite	$(\text{CaMg}) \text{CO}_3$	Rhombohedral	2.86	3.5	1.68	0.176	U-neg.	Equant	None
103. aragonite	Ca CO_3	Orthorhombic	2.94	3.5	1.68	0.155	B-neg.	Prismatic	None
104. witherite	Ba CO_3	Orthorhombic	4.3	3.5	1.68	0.148	B-neg.	Prismatic	None
Sulphides									
105. pyrite	Fe S_2	Cubic	5.02	6.5	—	—	—	Cubic	Opaque yellow
106. chalcopyrite	$(\text{Cu, Fe}) \text{S}_2$	Tetragonal	4.2	3.5	—	—	—	Prismatic	Opaque yellow
107. marcasite	Fe S_2	Orthorhombic	4.89	6	—	—	—	Tabular	Opaque yellow
108. galena	Pb S	Cubic	7.5	2.5	—	—	—	Cubic	Opaque grey
109. wurtzite	Zn S	Hexagonal	4.0	3.5	2.36	0.022	U-pos.	Prismatic	Yellow
Miscellaneous									
110. diamond	C	Cubic	3.3	10	2.42	—	Iso-tropic	Cubic	Yellow
111. graphite	C	Hexagonal	2.25	1	—	—	—	Lamellar	Opaque black
112. borax	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	Monoclinic	1.70	2	1.47	0.025	B-neg.	Prismatic	None
113. apatite	$\text{Ca}_5(\text{F, Cl})\text{P}_3\text{O}_{11}$	Hexagonal	3.2	5	1.64	0.004	U-neg.	Prismatic	Green, brown

X-RAY ANALYSIS

DIFFERENTIAL THERMAL ANALYSIS
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Three principal lines						Endothermic Peaks (maxima)		Exothermic Peaks (maxima)		
<i>d</i> in Å; <i>I</i> , relative intensity						Temp. °C.	Magnitude	Temp. °C.	Magnitude	
<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>					
4.29	10	3.06	7	2.87	7	225 350 960	large medium small	—	—	96
6.05	10	3.01	9	2.80	9	220 1020	large medium	—	—	97
2.98	10	1.89	6	4.93	5	570 795	large large	680	medium	98
2.74	10	1.697	9	2.099	8	760	v. large	—	—	99
2.78	10	1.728	8	2.127	6	545	medium	620	large	100
3.03	10	1.917	9	1.868	8	880	v. large	—	—	101
2.88	10	1.801	7	2.189	6	770 870	large large	—	—	102
3.40	10	1.98	10	2.70	8	820	v. large	—	—	103
3.58	10	1.91	9	2.56	9	840 983	large small	—	—	104
1.63	10	2.42	10	2.70	8	—	—	440	large	105
1.86	9	1.59	2	3.03	10	—	—	440 520	large medium	106
1.76	8	3.44	4	2.72	10	—	—	430	large	107
1.79	9	2.07	8	2.93	10	—	—	385	large	108
1.76	10	3.29	10	2.91	10	—	—	480	medium	109
2.06	10	1.26	8	1.07	6	—	—	—	—	110
3.37	10	2.03	6	1.16	5	—	—	820	v. large	111
2.57	10	2.81	9	4.83	7	150 410	v. large v. large	—	—	112
2.82	10	2.71	8	2.78	5	—	—	—	—	113

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